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## (54) APPARATUS AND METHOD FOR PRODUCING FULLERENE

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide an apparatus for continuously performing the production of a fullerene and the separation of the fullerene from another soot component in one apparatus and for continuously producing a large amount of fullerene and a method for producing the fullerene using it.

SOLUTION: The apparatus for producing the fullerene has a fullerene generating device to generate a gas stream which contains the fullerene, a polycyclic aromatic compound and a soot material containing a carbon base polymer component from a carbonous raw material and a separator to separate a gaseous fullerene and/or a gaseous polycyclic aromatic compound from the gas stream containing the soot material.

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(54) 【発明の名称】 フラーレンの製造装置およびフラーレンの製造方法

(57) 【要約】

【課題】 フラーレンの製造、及びフラーレンと他の炭素成分の分離を1つの装置内で連続的に行うことができ、且つ大量のフラーレンを連続的に生産することが出来る。フラーレンの製造装置およびこれを用いたフラーレンの製造方法を提供する。

【解決手段】 炭素質原料から、フラーレン、多環状芳香族化合物、及び炭素系高分子成分を含む炭状物質を含有する気流を生成させるフラーレン生成装置と、炭状物質を含有する気流から気体状態のフラーレン及び／又は気体状態の多環状芳香族化合物を分離する分離装置とを有するフラーレンの製造装置。

## 【特許請求の範囲】

【請求項1】 炭素質原料から、フラレーン、多環状芳香族化合物、及び炭素系高分子成分を含む煤状物質を含有する気流を生成させるフラレーン生成装置と、煤状物質を含有する気流から気体状態のフラレーン及び／又は気体状態の多環状芳香族化合物を分離する分離装置とを有するフラレーンの製造装置。

【請求項2】 更に、生成装置及び分離装置を減圧するための減圧装置を有し、フラレーン生成装置、分離装置、減圧装置がこの順に接続されていることを特徴とする請求項1記載のフラレーンの製造装置。

【請求項3】 更に、分離装置を通過した気体状態のフラレーンを析出させる析出装置を有し、フラレーン生成装置、分離装置、析出装置がこの順に接続され、減圧装置が析出装置の前又は後に設けられたことを特徴とする請求項1又は2に記載のフラレーンの製造装置。

【請求項4】 析出装置中にさらに、分子置に依りてフラレーンを分離する分離領域を設けたことを特徴とする請求項1乃至3のいずれかに記載のフラレーンの製造装置。

【請求項5】 分離装置が、煤状物質に含まれる気体状態のフラレーン及び／又は気体状態の多環状芳香族化合物を通過させるフィルターを有し、該フィルターの耐熱温度が300℃以上であることを特徴とする請求項1乃至4のいずれかに記載のフラレーンの製造装置。

【請求項6】 フラレーン生成装置におけるフラレーンの生成方法が、炭化水素原料を不完全燃焼させる燃焼法か、又は炭化水素原料を熱分解する熱分解法であることを特徴とする請求項1乃至5のいずれかに記載のフラレーンの製造装置。

【請求項7】 分離装置が、煤状物質含有気流から分離された炭素系高分子成分を回収する回収手段を有することを特徴とする請求項1乃至6のいずれかに記載のフラレーンの製造装置。

【請求項8】 以下の工程(1)及び工程(2)を有するフラレーンの製造方法。

工程(1)：炭化水素原料を不完全燃焼させるか、又は炭化水素原料を熱分解することにより、フラレーン、多環状芳香族化合物、及び炭素系高分子成分を含む煤状物質含有気流を生成させる工程。

工程(2)：工程(1)で得られた、フラレーン、多環状芳香族化合物、及び炭素系高分子成分を含む煤状物質含有気流から、フラレーン及び／又は多環状芳香族化合物を気体状態で分離する工程。

【請求項9】 工程(2)において多環状芳香族化合物を気体状態で分離し、次いで得られた、フラレーン及び炭素系高分子成分を含む煤状物質から、フラレーンを分離することを特徴とする請求項8に記載のフラレーンの製造方法。

【請求項10】 工程(1)で得られた400～150

0℃の煤状物質含有気流を、工程(2)で用いることを特徴とする請求項8または9に記載の製造方法。

【請求項11】 工程(2)にて多環状芳香族化合物を分離し得られた、フラレーン及び炭素系高分子成分を含む煤状物質から、芳香族炭化水素化合物を含む溶媒によりフラレーンを抽出し分離する工程を有することを特徴とする請求項9又は10に記載のフラレーンの製造方法。

【請求項12】 工程(2)にて多環状芳香族化合物を分離し得られた、フラレーン及び炭素系高分子成分を含む煤状物質含有気流から、フラレーンを気体状態で分離する工程を有することを特徴とする請求項9又は10に記載のフラレーンの製造方法。

【請求項13】 工程(2)を経て気体状態で得られたフラレーン及び多環状芳香族化合物を、冷却してこれらの固体状又は液体状混合物とし、この混合物から、フラレーンの溶解度が低く、且つ多環状芳香族化合物の溶解度の高い有機溶媒によって多環状芳香族化合物を抽出し分離する工程を有することを特徴とする請求項8に記載のフラレーンの製造方法。

【請求項14】 工程(2)を経て気体状態で得られたフラレーン及び多環状芳香族化合物を、冷却してこれらの固体状又は液体状混合物とし、この混合物を加熱して多環状芳香族化合物を気体状態で分離する工程を有することを特徴とする請求項8に記載のフラレーンの製造方法。

【請求項15】 工程(2)を経て気体状態で得られたフラレーン及び多環状芳香族化合物を冷却し、多環状芳香族化合物を気体状態としたまま、フラレーンを固体として分離する工程を有することを特徴とする請求項8に記載のフラレーンの製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、新しい炭素材料であるフラレーン、中でもC<sub>60</sub>、C<sub>70</sub>、C<sub>76</sub>、C<sub>84</sub>、C<sub>86</sub>、C<sub>90</sub>、C<sub>92</sub>、C<sub>94</sub>の分子構造を有するフラレーンの製造装置及び製造方法に関する。

## 【0002】

【従来の技術】 1990年に炭素数60、70、84等の閉殻構造型のカーボンクラスター（球状の巨大分子）という新しいタイプの分子状炭素物質が合成され、注目されている。この特殊な分子構造を有するカーボンクラスターはフラレーンとも称され、その分子骨格を構成する炭素数によって、フラレーンC<sub>60</sub>、同C<sub>70</sub>、同C<sub>84</sub>などと呼ばれている（単にC<sub>60</sub>、C<sub>70</sub>、C<sub>84</sub>等とも呼ばれる）。これらフラレーン類（以下、単に「フラレーン」と言う場合がある。）は新しい炭素材料であり、また特殊な分子構造から特異な物性を示すことが期待されるので、その性質及び用途開発についての研究が盛んに進められている。フラレーンは例えば、

ダイヤモンドコーティング、電池材料、塗料、断熱材、潤滑材、医薬品、化粧品などの分野への利用が期待されている。具体的には例えば以下に示す(1)～(4)の分野において革新的な用途開発が急速に展開されつつある。

【0003】(1)超硬材料への応用：フラーレンを前駆体とすることで微細結晶粒子をもつ人工ダイヤモンドの結晶が可能のため、付加価値のある耐摩耗材料への利用が期待されている。

(2)医薬品への応用：C<sub>60</sub>誘導体等を用いることで、抗癌剤、エイズ、骨粗鬆症、アルツハイマー治療薬、造影剤、及びステント材料等の用途としての研究が進められている。

(3)超伝導材料への応用：フラーレン薄膜に金属カリウムをドーピングすると、18Kという高い転移温度を持つ超伝導材料をつくり出すことができることが発見され、多方面から注目を集めている。

(4)半導体製造への応用：感光性樹脂(レジスト)にC<sub>60</sub>を混ぜることで、レジスト構造がより一層強化されることを利用し、次世代半導体製造への応用が期待されている。

【0004】フラーレンの製造方法としては、(1)グラファイトなど炭素質材料から成る電極を原料とし、この電極間にアーク放電を生じさせることで原料を蒸発させる方法(アーク放電法)、(2)炭素質原料に高電流を流して原料を蒸発させる方法(抵抗加熱法)、(3)高エネルギー密度のパルスレーザー照射によって、炭素質原料を蒸発させる方法(レーザー蒸発法)、及び(4)ベンゼンなどの有機物を不完全燃焼させる方法(燃焼法)などが知られている。

【0005】しかし、現状いずれの製造方法でも目的の単一フラーレン、あるいは有益なC<sub>60</sub>、～C<sub>70</sub>等のフラーレンだけを製造することはできず、C<sub>60</sub>及びC<sub>70</sub>を主とする複数のフラーレンと、その他多数の炭素化合物との混合物(この燃焼生成物は「煤状物質」と呼ばれることがある)を生成してしまう。この煤状物質中におけるフラーレンの含有量は、効率的といわれるアーク放電法でも10～30%程度である為、高純度のフラーレンを得るには、煤状物質からフラーレンを分離する必要がある。

【0006】煤状物質からのフラーレンの分離方法としては、例えば溶媒抽出法が知られている。これはフラーレンがベンゼン、トルエン、二硫化炭素等の有機溶媒に溶解するのに対し、その他の煤状物質の多くを占める、いわゆる「煤」である炭素系高分子成分はグラファイトやアモルファスカーボンに似て有機溶媒に溶解しにくい、という性質を利用した方法である。また煤状物質からフラーレンを分離する別の方法としては、高真空中で煤状物質を加熱し、フラーレンを昇華させる方法(昇華法)が知られている。この昇華法は、たとえば400℃

以上の高温、0.133Pa(10<sup>-3</sup>Torr)以下の高真空条件を必要とする特殊な分離方法であり、それに比べ溶媒抽出法は操作が容易なため広く用いられている。さらに抽出で得られたフラーレンは、主としてC<sub>60</sub>とC<sub>70</sub>のを含む溶液であり、この溶液から単一のフラーレンを分離するには、カラムクロマト分離、分別再結晶等の他に、フラーレンを包接化する方法等が適用されている。

【0007】その他、煤状物質からのフラーレン分離方法としては、C<sub>60</sub>を含有する煤状物質を有機溶媒により抽出して得られた、主としてC<sub>60</sub>を含む溶液を、活性炭と接触処理した後、得られた処理液から、有機溶媒を分離除去することにより、C<sub>60</sub>を精製する方法がある(例えば、特許文献1参照)。またフラーレンの分離精製装置としては、加熱容器、トラップ、減圧装置を含む、少量・バッチ式の分離精製装置が知られている。具体的には、フラーレンを加熱して昇華させるための加熱容器と、該加熱容器に接続されており、昇華したフラーレンを析出させるためのトラップと、加熱容器及びトラップの内部を減圧吸引するための減圧装置とを少なくとも備え、加熱容器、トラップ、減圧装置がこの順序で配設されているものである(例えば、特許文献2参照)。

【0008】

【特許文献1】特開平5-85711号公報

【特許文献2】特開平9-227111号公報

【特許文献3】米国特許第5273729号明細書

【0009】

【発明が解決しようとする課題】しかしこれらの分離精製方法は、いずれもバッチ式であり、少量の煤状物質を対象とした精製技術である。故に、大量の煤状物質を精製対象とする工業的規模でのフラーレン製造には不向きである。またこの煤状物質には、カーボンブラックに代表される様な、現在、工業的に価値の高い煤である炭素系高分子成分等が大量に含まれている。よって大量の煤状物質から、これら炭素系高分子成分をも有効に利用するためにも、炭素系高分子成分とフラーレンとを出来るだけ効率良く分離できる、フラーレンの製造装置及び製造方法の開発が望まれていた。

【0010】またフラーレンの製造方法においても、フラーレンと共に生成する多環状芳香族化合物が問題となっていた。具体的には例えば、制御された温度・圧力条件下でトルエン等の有機物を不完全燃焼させる方法(燃焼法)によってフラーレンを製造する場合、C<sub>60</sub>とC<sub>70</sub>を主とする複数のフラーレンを含んだ煤状物質が生成するが、この煤状物質には、10ppm～5重量%の多環状芳香族化合物が含まれていることが知られている(例えば、特許文献3参照)。

【0011】この多環状芳香族化合物は、ベンゾピレンに代表される様に、芳香族化合物の中でも組成的に水系

原子の割合が少なく、フラレーン類と類似している。従って、フラレーン類に混在している場合にはフラレーンの反応性を阻害したり、フラレーンの固有の性質に影響を与える可能性がある。また一般的にこれら多環状芳香族化合物は毒物であり、安全性の面から、極力低減する必要がある。

【0012】しかし、フラレーン類と多環状芳香族化合物の溶媒への溶解度を比較すると、一般的に多環状芳香族化合物の溶解度の方が10倍以上高い。その為、煤状物質を溶媒で抽出すると、フラレーン類のみを選択的に抽出することは困難で、煤状物質中の多環状芳香族化合物をも、殆ど抽出液へ同時に抽出してしまう。その為、この抽出液からフラレーンを固体として得るべく、例えば抽出液を濃縮・乾燥したり、抽出液を濃縮して析出した固形分を遠心乾燥して（主としてフラレーンを含む）固体を得たとしても、この固体中には、通常0.01～10%程度の多環状芳香族化合物が含まれてしまうという問題がある。本発明は前述した様な事情に鑑みてなされたものであり、フラレーンの大量製造の際、生成する大量の煤状物質からフラレーンを効率良く分離回収する製造装置および製造方法を提供することを目的とする。

【0013】

【課題を解決するための手段】一般的に、煤状物質中に大量の存在する炭素系高分子成分は、一度固体になると容易に気体状態へ変化しないのに対し、フラレーンは400℃以上の温度領域で気体状態へ変化することが知られている。

【0014】本発明者らは、フラレーンの昇華温度が400℃以上という比較的低温であることに着目した。そして特定のフラレーン製造方法、具体的には炭素質原料を用いた燃焼法や熱分解法においては、気流中に浮遊した状態、つまり煤状物質含有気流として煤状物質が得られ、且つこの気流は、通常、有る程度高温である為にフラレーンは気体状態で存在し、且つ炭素系高分子成分は固体状態にあると考えた。

【0015】そして本発明者らが鋭意検討した結果、この様な特定の手法により得られた煤状物質含有気流からは、有機溶媒を用いずとも、フラレーンの製造過程で大量に生ずる、いわゆる煤である炭素系高分子成分を含む煤状物質から、フラレーンを気体状態で分離できることを見出した。更に発明者らは、この煤状物質に含まれる大量有害な多環状芳香族化合物をも、気体状態で分離可能であることをも見出した。つまり、この多環状芳香族化合物の昇華温度はフラレーンのそれよりも低いので、燃焼法や熱分解法において得られた、フラレーン、多環状芳香族化合物、及び炭素系高分子成分を含む煤状物質含有気流を、まず多環状芳香族化合物が昇華する温度まで加熱して多環状芳香族化合物を気体状態で分離し、ついで更に煤状物質含有気流を加熱すること等で、フラ

レーンを気体状態で分離出来ることを見出し、本発明を完成させた。

【0016】即ち本発明の要旨は、炭素質原料から、フラレーン、多環状芳香族化合物、及び炭素系高分子成分を含む煤状物質を含有する気流を生成させるフラレーン生成装置と、煤状物質を含有する気流から気体状態のフラレーン及び／又は気体状態の多環状芳香族化合物を分離する分離装置とを有するフラレーンの製造装置に存する。

【0017】また本発明の今ひとつの要旨は、以下の工程（1）及び工程（2）を有するフラレーンの製造方法に存する。

工程（1）：炭化水素原料を不完全燃焼させるか、又は炭化水素原料を熱分解することにより、フラレーン、多環状芳香族化合物フラレーン、多環状芳香族炭化水素、及び炭素系高分子成分を含む煤状物質含有気流を生成させる工程。

工程（2）：工程（1）で得られた、フラレーン、多環状芳香族化合物、及び炭素系高分子成分を含む煤状物質含有気流から、フラレーン及び／又は多環状芳香族化合物を気体状態で分離する工程。

【0018】

【発明の実施の形態】先ず、フラレーンの製造装置について説明する。

【0019】図1はフラレーン生成装置において燃焼法を用いた場合の、本発明に係るフラレーン製造装置の一例の全体概略図である。本発明に係るフラレーン製造装置は、フラレーン生成装置1、フラレーンとその他の成分、具体的には多環状芳香族化合物や炭素系高分子成分とを分離する分離装置3を有する。好ましくは更に、フラレーンを析出させる析出装置5、及び減圧装置4を有する。フラレーンの生成に燃焼法を用いる場合、フラレーン生成装置1は、ヘリウム等の不活性ガスを充填させ、内部の圧力を大気圧に対して減圧条件、好ましくは真空に近い状態とした生成装置1である。該装置の側面に導入管（図示せず）から導入されたベンゼン等のフラレーン原料炭化水素を酸素と共にフラレーン生成装置1内に導入する。またフラレーン生成装置1内には、原料炭化水素を不完全燃焼を起こさせるためのバーナー2を少なくとも備える。このような構造により、連続的に、フラレーンを含む煤状物質を含む気流を製造することが出来る。本発明では、この煤状物質含有気流から、フラレーンを気体状態で分離すること、追って、且つ大量のフラレーンを製造する事が出来る。

【0020】フラレーン生成装置1の内部又は下流には、フラレーンの分離装置3が設置される。またフラレーンの生成、及びフラレーンを気体状態で分離するためには、一般的にフラレーン生成装置1内や、分離装置3内を減圧状態としておくことが好ましいので、フラレーンの生成装置1、分離装置3の内部圧力を減圧するため

の、源圧装置4を備えることが好ましい。本発明のフラーレンの製造装置では、フラーレンの生成装置からフラーレンを含む煤状物質含有気流が、分離装置3、析出装置5と流れるが、一般的にこの気流の流れは程やかなので、フラーレンを効率的に得るために、析出装置5に続いて源圧装置4を配設し、気流を効率的に流すことが好ましい。

【0021】分離装置3を構成する分能手段としては、従来公知のフィルター作用を有するものを使用できる。通常、フラーレンの生成は高温条件下で行われるので、そのようなフラーレンの生成装置1の次ぎに設けられる分離装置2に用いるフィルターとしては、耐熱性フィルターを用いる。耐熱フィルターは、400℃以上の温度で固体として存在する煤成分を捕集するための目的で設置され、フラーレンは、昇昇して気体状態で存在している温度領域に設置することが重要である。この様なフィルターとしては例えば、日本ポルセレン製焼結金属フィルターや富士フィルター社製焼結金属フィルター等が挙げられる。フィルター目開きの大きさは、フラーレンを生成させる燃焼条件や煤状物質の性状によって適宜選択し決定すればよい。フラーレンの昇昇温度は真空度によっても変化するので、容器内の真空度により、もっとも効率的にフラーレンを通過させることのできる位置に該フィルターを設置することが重要である。

【0022】この耐熱フィルターの材質は、300℃以上の高温に耐えられるものであれば何であってよく、セラミック、焼結金属等が好適に用いられる。また、このフィルターによって捕集される炭素系高分子成分が、連続的に排出される逆洗装置等の回収手段6を備えることが好ましい。この段階で得られた炭素系高分子成分は、インクや塗料等の着色剤、タイヤ用カーボンブラック、または燃料等として有効に活用できるものである。フラーレン生成装置1、や分離装置3を構成する素材は、上述の温度、圧力条件に耐えうるものであれば、その材質としては、例えば石英ガラス、ステンレス等の金属類、セラミックス、ガラス等が挙げられる。

【0023】また分離装置3における分離方法は、バッチ式、固定床型、流動層型、連続型等、任意のものを使用できる。そして分離装置3においては、フラーレン生成装置1より導入する気流に、不活性ガスを更に添加する場合がある。その際には、分離装置に不活性ガスの流入口及び排出口を設けておき、連続的または間欠的に不活性ガスを流入及び排出させればよい。また分離装置3に流入させる不活性ガスの温度を調整して、分離装置3内の温度を所定の温度に上昇または降下させても良い。この分離装置3にて、フラーレンと多環状芳香族化合物とを同時に、気体状態で分離しても良いが、この分離装置3の前に、分離装置3と同様な、多環状芳香族化合物を分離するための分離装置を設けても良い。この際、多環状芳香族化合物とフラーレンとは別個に、気体状態で

分離可能となる。

【0024】分離装置3を通過したフラーレンは、 $C_{60}$ 、や $C_{70}$ 、およびこれ以上の分子量を有する高次フラーレンを含む、いわゆる「粗なフラーレン」である。これを更にフラーレン分子量に応じて生成するには、これらの昇昇温度の差を利用すればよい。 $C_{60}$ 、や $C_{70}$ 、などのフラーレンは昇昇温度が異なるため、それぞれが気体状態から固体状態となる温度の位置にそれぞれ分離領域（図示せず）を設置することで $C_{60}$ 、と $C_{70}$ 、を分離捕集することが可能である。このような、分子量に応じてフラーレンを分離する分離領域は析出装置5内に設けるのが好ましい。分離領域としては、先述の分離装置3と同様なフィルターや、析出領域5内の温度を段階的に下げ、各フラーレンが析出装置5の内面壁等に順次析出させてもよい。最終的にはフラーレンの昇昇温度以下の温度になる位置にフィルター等を設置することで、フラーレンを捕集することができる。

【0025】続いて、本発明のフラーレンの製造方法について述べる。

#### 工程(1)

本発明の工程(1)においては、フラーレンを含む煤状物質含有気流を得る。この際、フラーレンは原料となる炭化水素（原料炭化水素）を不完全燃焼させる燃焼法、または高熱下に原料炭化水素を分解させる熱分解法によって製造する。よってフラーレン製造の際には、多環状芳香族化合物や炭素系高分子成分も同時に生ずるので、この煤状物質含有気流は、フラーレン、多環状芳香族化合物、及び炭素系高分子成分を含有する煤状物質を含む気流（煤状物質含有気流）となる。

【0026】燃焼法はフラーレンの大量生産に向き、またフラーレン合成域における最高温度が1700℃程度と他の方法と比べて比較的低温であり、またフラーレンが気相の状態で存在し、フラーレン以外の、特に煤状物質の多くを占める炭素系高分子成分が固体の状態で存在している温度領域が特定しやすく、フラーレンの分離を効率的に行えるので好ましい。燃焼法によりフラーレンを製造する場合、圧力条件としては大気圧に対して減圧下で行うのが一般的であり、減圧度は適宜選択すればよい。具体的な圧力条件としては1330～13300Pa（10～100Torr）が好ましく、更に3990～6650Pa（30～50Torr）が好ましい。温度条件としては、先述した圧力条件に応じて適宜選択すればよいが、中でも800～2500℃が好ましく、更に1000～2000℃、特に1200～1600℃であることが好ましい。

【0027】フラーレンの原料となる炭化水素としては、ベンゼン、トルエン、キシレン、ナフタレン、メチルナフタレン、アントラセン、フェナントレン等の炭素数6～20の芳香族炭化水素が好適に用いられる。また、原料炭化水素としては、これらの芳香族炭化水素に

併用してヘキサン、ヘプタン、オクタン等の脂肪族炭化水素を用いても良い。

【0028】燃焼法において用いる原料炭化水素は、同時に熱源としても作用する。即ちこの原料炭化水素は酸素と反応して発熱してフラレーンの生成が可能となる温度に上昇させるとともに、原料炭化水素が脱水素されることにより、フラレーン骨格を形成するための炭素ユニットを生成するものと考えられている。炭素ユニットは一定の圧力、温度条件で集合してフラレーン類を形成する。

【0029】また燃焼における燃料と空気の割合も適宜選択すればよいが、導入空気が理論燃焼するために必要な燃料と投入する燃料の比は、通常、常温、常圧での体積比において1:2~1:4、更には1:2~1:2.5であることが好ましい。燃焼法に於いて用いる酸素の使用量としては、原料炭化水素の種類によっても若干異なるが、例えば原料炭化水素としてトルエンを用いた場合には、トルエンに対して0.5~9倍モルが好ましく、1~5倍モルが更に好ましい。燃焼法における反応系には、酸素以外に、フラレーンに対して不活性ガスを存在させていても良い。本発明において不活性ガスとは、フラレーン類と実質的に反応しない気体を意味する。不活性ガスの種類としては、ヘリウム、ネオン、アルゴン、窒素及びこれらの混合物が挙げられる。

【0030】燃焼法により得られた煤状物質中には、フラレーン及び多環状芳香族炭化水素が含まれる。これら以外の残部は、通常、グラファイト構造を持つ炭素グラファイト構造を骨格として若干の水素原子を有する、高分子の炭化水素やカーボンブラック等（炭素系高分子成分）である。工程（1）にて得られる煤状物質には、フラレーン類が5重量%以上含まれていることが好ましく、更には10%以上、特に15%以上含まれていることが特に好ましい。また、本発明により製造されるフラレーン類は、フラレーン構造を有していれば炭素数に制限はないが、通常は炭素数60~84のフラレーンであり、中でもC<sub>70</sub>とC<sub>72</sub>の割合が全フラレーン中において50%以上であることが好ましく、更には70%以上、特に80%以上であることが好ましい。

【0031】工程（1）で得られる煤状物質含有気流は、通常、速度が緩やかで、300℃以上の温度を有するものである。この気流をそのまま次の工程（2）へ供しても良いし、例えば前述の不活性ガス流を供給して気流速度を上昇させ、工程（2）での効率を高めても良い。又必要に応じてこの煤状物質含有気流を加熱しても良い。この際、煤状物質含有気流の温度は、フラレーン及び/又は多環状芳香族化合物が気体で存在できる温度以上であればよく、具体的には400℃以上であることが好ましい。また煤状物質含有気流の温度が高すぎるとフラレーン製造装置への負荷が大きく、温度上昇に見合う効果の増加が少なくなるので、200℃以下、中で

も1500℃以下であることが好ましい。尚、本発明に於ける多環状芳香族化合物とは、少なくとも一つ以上の芳香環を有し、2環以上が縮合している芳香族化合物を示す。多環状芳香族化合物の具体例としては、ナフタレン、アントラセン、フェナントレン、ベンゾピレン等が挙げられる。

【0032】（工程2）工程（2）では、前述の工程（1）で得られた、フラレーン、多環状芳香族化合物及び炭素系高分子成分を含む煤状物質含有気流から、フラレーン及び/又は多環状芳香族化合物を気体状態で分離する。分離の方式としては、以下の（工程2-1）、（工程2-2）が挙げられる。

（工程2-1）まず、煤状物質含有気流から、気体状態で多環状芳香族化合物を分離する。次にフラレーンと炭素系高分子成分との混合物から、フラレーンを分離する方法。

（工程2-2）まず気体状態のフラレーンと気体状態の多環状芳香族化合物を、炭素系高分子成分等の煤状物質に含まれる他の物質と分離し、次にフラレーンと多環状芳香族化合物との混合物から、フラレーンを分離する方法。これらの工程について説明する。

【0033】（工程2-1）この工程では、煤状物質含有気流から、気体状態で多環状芳香族化合物を分離する。この際の分離条件としては、多環状芳香族化合物が気体状態で存在できれば、任意の温度、圧力条件を適宜選択すればよく、経済性を考えて、最適な条件で実施すればよい。一般的に圧力は100~2×10<sup>5</sup> Paが好ましく、更には1000~1.4×10<sup>5</sup> Paであることが好ましい。常圧では装置が簡単になるメリットがあり、減圧下では分離条件温度が低くても多環状芳香族化合物が気体状態で存在するので分離が可能であり、経済的メリットがある。

【0034】また分離条件温度は、圧力にもよるが、好ましくは100℃以上600℃以下である。多環状芳香族化合物が気体状態で存在できる温度は、当然、圧力によって変化するので、分離条件温度は適宜選択すればよい。分離条件温度が高圧の場合には、更に200℃以上600℃以下が好ましく、特に300℃以上550℃以下が好ましい。温度が低すぎると多環状芳香族炭化水素が固体として析出する場合があります。逆に温度が高すぎるとフラレーンも気体状態となるので多環状芳香族化合物とともに分離されてしまい、フラレーンの回収率が低下する場合があります。

【0035】多環状芳香族化合物の分離に際しては、工程（1）で得られた煤状物質含有気流をそのまま用いても良いが、前述のような不活性ガスを、更に添加しても良い。これら不活性ガスとフラレーンとの反応を避けるためには、分離装置内を実質的に不活性ガスにより置換し、不活性ガス流通下で多環状芳香族化合物の分離を行うことが好ましい。中でも分離装置内における気体中の



酸素含有量を10体積%以下とするのが好ましく、更には5体積%以下、特に1体積%とするのが好ましい。酸素含有量が多いとフラレーンの酸化物が生成する場合があり、フラレーンの収率が低下する場合がある。

【0036】多環状芳香族化合物の分餾の際、不活性ガスの流通量としては、フラレーン及び多環状芳香族炭化水素を含む炭状物質1gに対して、工程(1)から待ち込まれる不活性ガス量との合計が、1~10000ml/minであることが好ましく、更には5~5000ml/minであることが好ましい。不活性ガスの流通は連続的であっても間欠的であってもよい。分餾装置で分餾された多環状芳香族化合物は、気流に伴って、例えば析出装置にて温度が下げられることによって、固体の多環状芳香族化合物として回収すればよい。この析出装置は、分餾装置と同一装置内に設けても、また別の装置として設けてもよい。この多環状芳香族化合物の回収は、バッチ式または連続式のいずれでもよい。析出した多環状芳香族化合物の回収は、そのまま固体として、又は溶媒に溶解して回収してもよい。

【0037】多環状芳香族化合物の析出、回収の方法は、従来公知の、気体状態物質を固化させて回収する技術を用いればよい。例えば、冷却した回転ドラムに気体状態の多環状芳香族化合物を含有するガスを接触させて多環状芳香族化合物を析出させ、間欠的もしくは連続的にスクレーパーで掻き取り回収する方法が挙げられる。また、回転ドラムをに付着した多環状芳香族炭化水素を有機溶媒により溶解し除去・回収してもよい。また別の方法としては、気体状態の多環状芳香族化合物を、水又は有機溶媒のスプレーゾーンを通過させるか、又は気体状態の多環状芳香族化合物を含むガスを、水又は有機溶媒中へ吹き込むことでガスを冷却し、多環状芳香族化合物を析出（あるいは有機溶媒に溶解させて）回収する方法が挙げられる。この際、水中に多環状芳香族化合物を析出させて回収した際には、さらに有機溶媒で多環状芳香族化合物を抽出すればよい。

【0038】工程(2-1)で多環状芳香族化合物を分離した後、フラレーンと炭素系高分子成分の混合物からフラレーンを分餾する。フラレーンと炭素系高分子成分とを分離する方法は特に制限はないが、例えばフラレーンと炭素系高分子成分を含む炭状混合物を抽出溶媒と混合して、フラレーンが溶解した抽出液を得る方法（工程2-1-1）と、フラレーン及び炭素系高分子成分を含む炭状混合物を、不活性ガス等の存在下で加熱し、フラレーンを昇気分餾する方法（工程2-1-2）が挙げられる。

【0039】（工程2-1-1）フラレーンを溶解した抽出液を得る場合の抽出溶媒としては、好ましくは芳香族炭化水素を含む溶媒が用いられる。芳香族炭化水素としては、分子内に少なくとも1つのベンゼン核を有する炭化水素化合物であり、具体的にはベンゼン、トルエ

ン、キシレン、エチルベンゼン、*n*-プロピルベンゼン、イソプロピルベンゼン、*n*-ブチルベンゼン、*sec*-ブチルベンゼン、*tert*-ブチルベンゼン、1,2,3-トリメチルベンゼン、1,2,4-トリメチルベンゼン、1,3,5-トリメチルベンゼン、1,2,3,4-テトラメチルベンゼン、1,2,3,5-テトラメチルベンゼン、ジエチルベンゼン、シメン等のアルキルベンゼン類、1-メチルナフタレン等のアルキルナフタレン類、テトラリン等が挙げられる。これらの内1,2,3-トリメチルベンゼン、1,2,4-トリメチルベンゼン及びテトラリンが好ましい。

【0040】抽出溶媒としては上述した芳香族炭化水素の他に、更に脂肪族炭化水素や塩素化炭化水素等の有機溶媒を、単独又はこれらのうち2種以上を任意の割合で用いてもよい。脂肪族炭化水素としては、環式、非環式等、任意の脂肪族炭化水素が使用できる。環式脂肪族炭化水素の例としては、単環式、多環式のものが挙げられ、例えば単環式ではシクロペンタン、シクロヘキサン、シクロヘプタン、シクロオクタンなどが挙げられる。また単環式脂肪族炭化水素の誘導体であるメチルシクロペンタン、エチルシクロペンタン、メチルシクロヘキサン、エチルシクロヘキサン、1,2-ジメチルシクロヘキサン、1,3-ジメチルシクロヘキサン、1,4-ジメチルシクロヘキサン、イソプロピルシクロヘキサン、*n*-プロピルシクロヘキサン、*t*-ブチルシクロヘキサン、*n*-ブチルシクロヘキサン、イソブチルシクロヘキサン、1,2,4-トリメチルシクロヘキサン、1,3,5-トリメチルシクロヘキサン等も挙げられる。多環式としては、デカリンなどが挙げられる。非環式脂肪族炭化水素の例としては、*n*-ペンタン、*n*-ヘキサン、*n*-ヘプタン、*n*-オクタン、イソオクタン、*n*-ノナン、*n*-デカン、*n*-ドデカン、*n*-テトラデカンなどが挙げられる。

【0041】塩素化炭化水素としては、シクロロメタン、クロロホルム、四塩化炭素、トリクロロエチレン、テトラクロロエチレン、1,2-ジクロロエタン、1,1,2,2-テトラクロロエタン、クロロベンゼン、ジクロロベンゼン、1-クロロナフタレンなどが挙げられる。その他、炭素数6以上のケトン、炭素数6以上のエステル類、炭素数6以上のエーテル類、二硫化炭素等を用いてもよい。

【0042】抽出溶媒におけるフラレーンの溶解度が低すぎるとフラレーンの抽出効率が低下するので、フラレーンの溶解度としては5g/リットル以上であることが好ましく、更には10g/リットル以上、特に15g/リットル以上であることが好ましい。また、工業的観点から、これらの抽出溶媒の中でも常温液体で沸点が100~300℃、中でも120~250℃のものが好適である。

【0043】抽出溶媒は、フラレーンを十分に抽出でき

るだけの量を用いる必要がある。通常、煤状混合物中のフラレーン含有量に対し、5～400重量倍量、経済性を考えると、40～200重量倍量程度使用するのが好ましい。抽出は、バッチ式、セミ連続式、連続式、又はそれらの組み合わせ等、形式、装置は特に限定されない。なお、煤状混合物には通常5～30重量%のフラレーンが含まれているが、抽出効率の観点から、フラレーンに対して用いる抽出溶媒の量を上述した範囲とするのが好ましいことから、抽出操作に先立って、煤状物質の一部を分析して、煤状物質中のフラレーン含有量を測定

しておくのが好ましい。  
【0044】抽出装置としては従来混合槽が好適に使用できる。抽出の際、容器内の圧力は特に制限はなく、常圧で実施すればよい。抽出時の温度としては通常-10～150℃であり、好ましくは5～80℃であり、更に好ましくは30～50℃である。これら範囲であれば抽出効率向上の面から好ましいが、抽出効率は温度依存性が小さいのでエネルギーコスト的に常温程度で行うのが有利である。抽出工程においては、更に必要に応じて、抽出液に超音波等を照射しながら抽出を行うと、抽出時間

間が短くなるので好ましい。  
【0045】こうして得られた抽出液には、フラレーンが溶解しており、また、多環芳香族化合物は前の工程（工程（2-1））にて既に除去されているので、抽出液から用いた有機溶媒等を留去すること等により、高純度のフラレーンを得ることが出来る。尚、フラレーンを抽出した後に残ったスラリーには、工業上有用な炭素系高分子成分が含まれている。よってこのスラリーから、未溶解物を濾別し、再利用することが可能である。濾別は、減圧濾過、加圧濾過、重力濾過、フィルター濾過、又はそれらの組み合わせ等、方法、装置は特に限定されないが、中でも加圧濾過が好ましい。

【0046】（工程2-1-2）多環芳香族化合物が分離された、フラレーンと炭素系高分子成分を含む煤状混合物は、多環芳香族化合物を気体状態で分離した際の温度よりも、高温条件下に付すことにより、フラレーンを気体状態で煤状混合物から分離できる。一般的に、多環芳香族化合物を分離した後、フラレーンは固体となっているので、煤状混合物を加熱することでフラレーンを昇気し分離できる。

【0047】昇華する際の条件は、常圧もしくは5000Pa程度の減圧下で実施する。常圧では装置が簡単になるメリットがあり、減圧下ではフラレーンの昇華温度が低くなるメリットがある。経済性を考えて、最適な条件で実施すればよい。窒素又はヘリウム等の不活性ガスを、煤状混合物1gに対し、前の工程から持ち込まれる不活性ガス量との合計が1～10000ml/min程度、好ましくは5～5000ml/min程度であることが好ましい。不活性ガスの流通は連続的であっても間欠的であってもよい。

【0048】置換が十分に実施されないと、フラレーンの酸化物が生成する場合がある。昇華を実施する際の不活性ガスは、予熱しても良いし、予熱しなくても良い。昇華に用いる装置は、バッチ式、固定床型、流動層型、連続型等特に限定はしない。この工程では、煤状混合物又はこれを含む気流から、気体状態でフラレーンを分離する。この際、分離条件としては、フラレーンが気体状態で存在できれば、任意の温度、圧力条件を適宜選択すればよく、経済性を考えて、最適な条件で実施すればよい。一般的に圧力は5000Pa程度の減圧下で行うのが好ましい。常圧では装置が簡単になるメリットがあり、減圧下では分離条件温度が低くてもフラレーンが気体状態で存在するので分離が可能であり、経済的メリットがある。

【0049】また分離条件温度は、圧力にもよるが、通常400℃～1400℃、更には600～1200℃、特に800℃～1100℃であることが好ましい。フラレーンが気体状態で存在できる温度は、当然、圧力によって変化する。分離条件温度は適宜選択すればよい。温度が低すぎるとフラレーンが充分気体状態とならないので収率が低下する場合があり、逆に温度が高すぎると経済的に不利になるばかりか、僅かな酸素が存在している場合などは、この酸素がフラレーンと反応してしまい、酸化物となってしまい、フラレーンの収率が低下する場合がある。

【0050】（工程2-2）次に、気体状態のフラレーンと、気体状態の多環芳香族化合物を、炭素系高分子成分等の煤状物質に含まれる他の物質と分離し、次にフラレーンと多環芳香族化合物との混合物から、フラレーンを分離する方法について説明する。この工程（2-2）では、工程（1）で得られた、フラレーン、多環芳香族化合物、及び炭素系高分子成分を含む煤状物質含有気流を、先述の工程（2-1-2）の条件下に付すことで、フラレーンと多環芳香族化合物とを、この煤状物質含有気流から気体状態で分離することが出来る。この際、分離条件は、先述の工程（2-1-2）と同様である。この様に分離された、気体状態の、フラレーンと多環芳香族化合物は、一般的にこれらを冷却して固体状又は液体状の混合物とする。ついで、例えば以下に示す工程（2-2-1）、工程（2-2-2）及び工程（2-2-3）の様な方法によって、フラレーンと多環芳香族化合物とを分離すればよい。

【0051】工程（2-2-1）

工程（2-2）を経て、気体状態で得られたフラレーン及び多環芳香族化合物を、冷却してこれらの固体状又は液体状混合物とし、この混合物を加熱して多環芳香族化合物を気体状態で分離する工程。

工程（2-2-2）

工程（2-2）を経て気体状態で得られたフラレーン及び多環芳香族化合物を冷却し、多環芳香族化合物を

気体状態としたまま、フラレーンを固体として分餾する工程。

#### 工程(2-2-3)

工程(2-2)を経て、気体状態で得られたフラレーン及び多環状芳香族化合物を、冷却してこれらの固体状又は液体状混合物とし、この混合物から、フラレーンの溶解度が低く、且つ多環状芳香族化合物の溶解度の高い有機溶媒によって多環状芳香族化合物を抽出し、分餾する工程。これら各工程について説明する。

#### 【0052】工程(2-2-1)

工程(2-2-1)においては、気体状態で得られたフラレーン及び多環状芳香族化合物(気体)を、冷却してこれらの固体状又は液体状混合物とする。そしてこの混合物を加熱し、フラレーンと多環状芳香族化合物を分離する。この分離の条件としては、フラレーンと多環状芳香族化合物とを気体状態で分離できれば、任意の温度、圧力をとることができる。例えば前述の工程(2-1)における、煤状物質含有気流から気体状態で多環状芳香族化合物を分離する際と同様の温度、圧力条件下で、フラレーンと多環状芳香族化合物とを気体状態で分離すればよい。この際の温度、圧力条件は、経済性を考えて、最適な条件で実施すればよい。中でも、前述の工程(2-1)における、煤状物質含有気流から気体状態で多環状芳香族化合物を分離する際と同様の温度、圧力条件における好ましい範囲とすることが、この工程(2-2-1)においても好ましい。

#### 【0053】工程(2-2-2)

工程(2-2-2)においては、気体状態で得られたフラレーン及び多環状芳香族化合物(気体)を、多環状芳香族化合物だけが気体状態となるように、つまりフラレーンが固体状又は液体状となり、気体状態の多環状芳香族化合物と分離できる状態にまで冷却し、フラレーンと多環状芳香族化合物とを分離する。この分離の条件としては、フラレーンが固体状又は液体状となり、且つ多環状芳香族化合物が気体状態で存在できれば、任意の温度、圧力をとることができる。例えば前述の工程(2-1)における、煤状物質含有気流から気体状態で多環状芳香族化合物を分離する際と同様の温度、圧力条件下で、フラレーンを固体状又は液体状として、多環状芳香族化合物を分離すればよい。この際の温度、圧力条件は、経済性を考えて、最適な条件で実施すればよい。中でも、前述の工程(2-1)における、煤状物質含有気流から気体状態で多環状芳香族化合物を分離する際と同様の温度、圧力条件における好ましい範囲とすることが、この工程(2-2-2)においても好ましい。

#### 【0054】工程(2-2-3)

この工程(2-2-3)では、フラレーン及び多環状芳香族化合物を含む固体状又は液体状混合物から、フラレーンの溶解度が低く、且つ多環状芳香族化合物の溶解度の高い有機溶媒を抽出溶媒として用い、多環状芳香族化

合物を抽出する工程である。この抽出溶媒、つまりフラレーン類の溶解度が低い溶媒(以下、貧溶媒と称することがある)の具体例としてはメタノール、エタノール、プロパノール、エチレングリコール、グリセリン等の炭素数1~4のアルコール類;アセトン、メチルエチルケトン等の炭素数3~5のケトン類;テトラヒドロフラン、ジエチルエーテル、ジオキサン等の炭素数2~5のエーテル類;N、N-ジメチルホルムアミド等の炭素数3~5のアミド類及びこれらを含む混合溶媒が挙げられる。これらの内、アルコール類が好ましく、なかでも炭素数3以下のものが好ましく、特に2-プロパノール(イソプロピルアルコール)が好ましい。

【0055】これら貧溶媒のフラレーンC<sub>60</sub>の溶解度としては、1g/リットル以下であることが好ましく、更には100mg/リットル以下、特に50mg/L以下であることが好ましい。貧溶媒は直接、前述の固体状又は液体状混合物と接触させても良いが、一般的には、この混合物を一旦、フラレーン及び多環状芳香族化合物の双方が高い溶解性を示す有機溶媒に溶解して溶液とし、これに貧溶媒を添加してフラレーンを析出させる。

【0056】この際の貧溶媒の使用量は、この溶液調整に用いた有機溶媒量に対し、0.1~50重量倍量、中でも1~30重量倍量程度であることが好ましい。貧溶媒の量が少ないと、フラレーンの析出量が少なくなり、回収できるフラレーンが減少する。多すぎると、これらの操作を行う容器容量が大きくなり、経済的にロスが発生する。貧溶媒を混合する温度としては、通常、-20~150℃であり、中でも-10~100℃、更には10~80℃、特に30~60℃であることが好ましい。貧溶媒を混合することにより析出したフラレーンは、濾過等により回収すればよい。一方、多環状芳香族炭化水素の殆どは析出せずに溶媒中に溶解しているので、フラレーン類を取り除いた後の溶液は、その溶媒を留去すること等により多環状芳香族化合物を固体として回収することが出来る。

#### 【0057】

【実施例】以下に実施例を示し、本発明を更に具体的に説明するが、本発明の要旨を越えない限り、本発明は以下の実施例に限定されるものではない。

#### 【0058】

【実施例1】トルエンを原料として燃焼法により得られた煤状物質3.8mgを、熱重量測定装置(セイコー社製TG-DTA6300)を用い、乾燥窒素ガス100cc/min中で、室温より20℃毎分に1150℃まで加熱し、重量の変化を測定した。得られた結果を図2に示す。図2において、左縦軸は、重量3.8mgに対する減重量率を、右縦軸は原料率の変化率を、横軸は加熱温度を示す。図2に示した、重量減少を示すグラフ、及び重量変化率を示すグラフから明らかな通り、温度が100℃以上となると重量が徐々に減少し、400

℃付近から重量減少が加速されていることが判る。そして500℃以上の高温領域に於いて煤状物質の重量が急激に減少する。これはフラレーンの昇華温度が400～800℃である事を考慮すると、煤状物質中の多量のフラレーンが昇華することで、煤状物質の急激な重量減少が\*

生じたことが判る。

【0059】更に、四重極形質量分析装置（日本電子製オートマスAM2-15型）を用い、煤状物質を加熱した際に発生したガス成分の定性分析を以下の条件で行った。結果を図3に示す。

測定法	: EI法
ファーンズ部温度	: 290℃
トランスファーチューブ温度	: 285℃
GCオープン温度	: 285℃
インターフェース温度	: 285℃
イオン化室温度	: 260℃
フォトマル電圧	: 450V
イオン化電圧	: 70eV
イオン化電流	: 300μA
マスレンジ	: 10～400amu
スキンスピード	: 1000msec

【0060】図3において、縦軸はイオンスペクトルの相対強度を、横軸は加熱温度を示す。図3より、煤状物質を加熱して発生したガス中には、ベンゼン（分子量78）、トルエン（分子量92）、キシレン（分子量106）等の芳香族化合物や、ナフタレン（分子量128）、アントラセン（分子量178）等の多環状芳香族化合物の存在を示すピークが、フラレーンの昇華温度より低い温度範囲に於いて確認された。これによって、ベンゼン等の芳香族化合物はもちろん、多環状芳香族化合物も気体状態で分離できることが判る。以上の実施例により、燃焼法によって得られた、フラレーン、多環状芳香族化合物、及び炭素系高分子成分を含む煤状物質から、フラレーン及び/又は多環状芳香族化合物を気体状態で分離出来る。よってこのような煤状物質を含有する気流から、フラレーン及び/又は多環状芳香族化合物を、連続的に、気体状態で分離することが可能であり、そしてこの煤状物質を含む気流から、連続的にフラレーンを分離可能であることが判る。

【0061】

【発明の効果】以上説明した本発明によれば、フラレーン※

の製造、フラレーンと他の煤成分の分離を1つの装置内で連続的に行うことができ、且つ大量のフラレーンを連続的に生産することが可能となる。次世代を担う新材料、新素材として多方面から注目されているフラレーンを工業的規模で製造した場合、同時に大量の生成される煤状物質とフラレーンを効率良く分離、回収することが出来る。

【図面の簡単な説明】

【図1】本発明に係るフラレーン合成分離装置の一例の全体概略断面図。

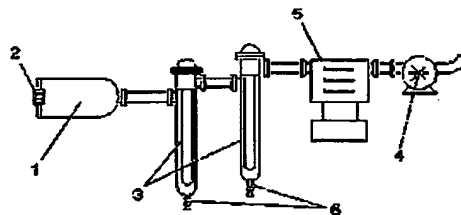
【図2】煤状物質を加熱した際の重量減少を示した図。

【図3】煤状物質を加熱した際に発生したガスの定性分析結果を示す図。

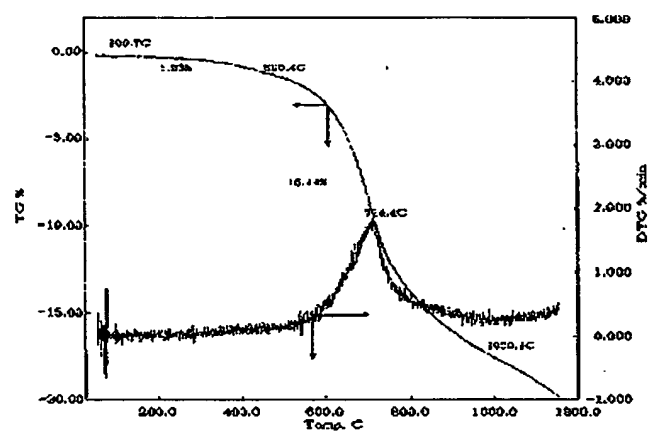
【符号の説明】

- 1: フラレーン生成装置
- 2: バーナー
- 3: 分離装置
- 4: 減圧装置
- 5: 析出装置
- 6: 回収装置

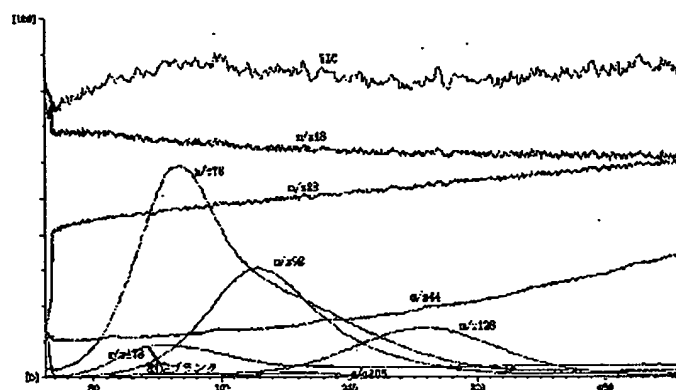
【図1】



【図2】



【図3】



フロントページの続き

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Fターム(参考) 4G146 AA08 BA12 BC02 BC03 BC27  
BC38A BC38B CA11 DA02  
DA03 DA08 DA27 DA28

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**CLAIMS**

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[Claim(s)]

[Claim 1] The manufacturing installation of the fullerene which has the decollator which separates the fullerene of a gaseous state, and/or the multi-annular aromatic compound of a gaseous state from the air current which contains fullerene, a multi-annular aromatic compound and the fullerene generation equipment that makes the air current containing the soot-like matter containing a carbon system macromolecule component generate, and the soot-like matter from a carbonaceous raw material.

[Claim 2] Furthermore, the manufacturing installation of the fullerene according to claim 1 characterized by having a decompression device for decompressing generation equipment and a decollator, and connecting fullerene generation equipment, the decollator, and the decompression device to this order.

[Claim 3] Furthermore, it is the manufacturing installation of the fullerene according to claim 1 or 2 to which it has deposit equipment which deposits the fullerene of a gaseous state which passed the decollator, fullerene generation equipment, a decollator, and deposit equipment are connected to this order, and a decompression device is characterized by preparing the front stirrup of deposit equipment behind.

[Claim 4] The manufacturing installation of the fullerene according to claim 1 to 3 further characterized by preparing the isolation region which separates fullerene according to molecular weight into deposit equipment.

[Claim 5] The manufacturing installation of the fullerene according to claim 1 to 4 which has the filter with which a decollator passes the fullerene of the gaseous state included in the soot-like matter, and/or the multi-annular aromatic compound of a gaseous state, and is characterized by the heat-resistant temperature of this filter being 300 degrees C or more.

[Claim 6] the combustion method to which the generation method of the fullerene in fullerene generation equipment carries out the incomplete combustion of the hydrocarbon raw material -- or the manufacturing installation of the fullerene according to claim 1 to 5 characterized by being the thermal decomposition method which pyrolyzes a hydrocarbon raw material.

[Claim 7] The manufacturing installation of the fullerene according to claim 1 to 6 to which a decollator is characterized by having a recovery means to collect the carbon system macromolecule components separated from the soot-like matter content air current.

[Claim 8] The manufacture approach of the fullerene which has the following processes (1) and processes (2).

Process (1): The process which makes the soot-like matter content air current which contains fullerene, a multi-annular aromatic compound, and a carbon system macromolecule component by carrying out the incomplete combustion of the hydrocarbon raw material, or pyrolyzing a hydrocarbon raw material generate.

Process (2): The process which separates fullerene and/or a multi-annular aromatic compound from the fullerene and the multi-annular aromatic compound which were obtained at the process (1), and the soot-like matter content air current containing a carbon system macromolecule component by the gaseous state.

[Claim 9] The manufacture approach of the fullerene according to claim 8 characterized by separating fullerene from the soot-like matter containing the fullerene and the carbon system macromolecule component which separated the multi-annular aromatic compound by the gaseous state in the process (2), and were subsequently obtained.

[Claim 10] The manufacture approach according to claim 8 or 9 characterized by using the 400-1500-degree C soot-like matter content air current acquired at the process (1) at a process (2).

[Claim 11] The manufacture approach of the fullerene according to claim 9 or 10 characterized by having the process which extracts fullerene with the solvent containing an aromatic hydrocarbon compound, and is separated from the soot-like matter containing the fullerene and the carbon system macromolecule component from which the multi-annular aromatic compound might be separated at the process (2).

[Claim 12] The manufacture approach of the fullerene according to claim 9 or 10 characterized by having the process which separates fullerene by the gaseous state from the soot-like matter content air current containing the fullerene and the carbon system macromolecule component from which the multi-annular aromatic compound might be separated at the process (2).

[Claim 13] The manufacture approach of the fullerene according to claim 8 which cools, uses as such shape of a solid-state and liquid mixture the fullerene and the multi-annular aromatic compound which were obtained by the gaseous state through the process (2), and is characterized by having the process which the solubility of fullerene extracts a multi-annular aromatic compound, and separates from this mixture with an organic solvent with the high solubility of a multi-annular aromatic compound low.

[Claim 14] The manufacture approach of the fullerene according to claim 8 which cools, uses as such shape of a solid-state and liquid mixture the fullerene and the multi-annular aromatic compound which were obtained by the gaseous state through the process (2), and is characterized by having the process which heats this mixture and separates a multi-annular aromatic compound by the gaseous state.

[Claim 15] The manufacture approach of the fullerene according to claim 8 characterized by having the process which separates fullerene as a solid-state, cooling the fullerene and the multi-annular aromatic compound which were obtained by the gaseous state through the process (2), and making a multi-annular aromatic compound into a gaseous state.

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[Translation done.]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing installation and the manufacture approach of the fullerene which is a new carbon material, and the fullerene which has the molecular structure of C60, C70, C76, C78, C82, and C84 especially.

[0002]

[Description of the Prior Art] The molecule-like carbon matter new type called the carbon cluster (spherical macromolecule) of the closed shell structured type of carbon numbers 60 and 70 and 84 grades is compounded, and attracts attention in 1990. The carbon cluster which has this special molecular structure is also called fullerene, and is called fullerene C60, this C70, this C84, etc. by the carbon number which constitutes that molecule frame (only called C60, C70, and C84 grade). These fullerene (it may only be hereafter called "fullerene") is new carbon materials, and since it is expected that unique physical properties will be shown from the special molecular structure, research on the property and application development is advanced briskly. As for fullerene, use in fields, such as for example, diamond coating, a cell ingredient, a coating, a heat insulator, lubricant, drugs, and cosmetics, is expected. In the field of (1) - (4) specifically shown below, innovative application development is being developed quickly.

[0003] (1) Application to a superhard ingredient : since purification of the artificial diamond which has a fine crystal grain child by using fullerene as a precursor is possible, use to an abrasion resistance material with added value is expected.

(2) Application to drugs : by using C60 derivative etc., research as an application of an anticancer agent, an acquired immunodeficiency syndrome, osteoporosis, the Alzheimer remedy, a contrast medium, a stent ingredient, etc. is advanced.

(3) Application to a superconducting material : if metallic potassium is doped to a fullerene thin film, it is discovered that a superconducting material with a high transition temperature called 18K can be made, and since various, attract attention.

(4) Application to semi-conductor manufacture : by mixing C60 with a photopolymer (resist), it uses that resist structure is strengthened further and the application to next-generation semi-conductor manufacture is expected.

[0004] As the manufacture approach of fullerene, the electrode which consists of carbonaceous ingredients, such as (1) graphite, is used as a raw material. By the pulse laser exposure of the approach (arc discharge method) of evaporating a raw material by making inter-electrode [ this ] producing arc discharge, the method (resistance heating method) of passing a high current in (2) carbonaceous raw materials, and evaporating a raw material, and (3) high-energy consistency The approach (combustion method) of carrying out the incomplete combustion of the organic substance, such as a method (laser evaporation method) of evaporating a carbonaceous raw material and (4) benzene, etc. is learned.

[0005] however, the present condition -- two or more fullerene which cannot manufacture only the target single fullerene or fullerene of useful C60 - useful C84 grade, but is mainly concerned with C60 and



C70 by any manufacture approach -- in addition, mixture (this products of combustion may be called the "soot-like matter") with many carbon compounds will be generated. Since it is about 10 - 30% also by the arc discharge method said for the content of the fullerene in this soot-like matter to be efficient, in order to obtain the fullerene of a high grade, it is necessary to separate fullerene from the soot-like matter.

[0006] As the separation approach of the fullerene from the soot-like matter, the solvent extraction method is known, for example. The carbon system giant-molecule component which occupies many of other soot-like matter to fullerene dissolving this in organic solvents, such as benzene, toluene, and a carbon disulfide, and which is the so-called "soot" is an approach using the property to be hard to dissolve in an organic solvent like graphite or amorphous carbon. Moreover, as an option which separates fullerene from the soot-like matter, the soot-like matter is heated under a high vacuum and the approach (the sublimating method) to which fullerene is made to sublimate is learned. This sublimating method is the special separation approach which needs an elevated temperature 400 degrees C or more and the high vacuum conditions below 0.133Pa (10<sup>-3</sup>Torr), and since a solvent extraction method is easy to operate it compared with it, it is used widely. The fullerene furthermore obtained by the extract is a solution which mainly contains that of C60 and C70, and in order to separate single fullerene from this solution, the approach of carrying out clathration of the fullerene else [, such as column chromatography separation and judgment recrystallization, ] etc. is applied.

[0007] In addition, after carrying out contact processing of the solution which extracted the soot-like matter containing C60 with the organic solvent as the fullerene separation approach from the soot-like matter, and was obtained and which mainly contains C60 with activated carbon, there is a method of refining C60 by carrying out separation removal of the organic solvent from the obtained processing liquid (for example, refer to patent reference 1.). Moreover, as a separation refiner of fullerene, the separation refiner of the small quantity and batch type containing a heating container, a trap, and a decompression device is known. It specifically connects with the heating container and this heating container for making fullerene heat and sublimate, and has a decompression device for carrying out reduced pressure suction of the interior of the trap for depositing the sublimated fullerene, and a heating container and a trap at least, and the heating container, the trap, and the decompression device are arranged in this sequence (for example, refer to patent reference 2.).

[0008]

[Patent reference 1] JP,5-85711,A [the patent reference 2] JP,9-227111,A [the patent reference 3] U.S. Pat. No. 5273729 specification [0009]

[Problem(s) to be Solved by the Invention] However, each of these separation purification approaches is batch types, and is the purification techniques for the little soot-like matter. Therefore, it is unsuitable for fullerene manufacture on the industrial scale which makes a lot of soot-like matter applicable to purification. Moreover, current [ which is represented by carbon black ], the carbon system macromolecule component which is worthy soot industrially are contained in this soot-like matter in large quantities. Therefore, from a lot of soot-like matter, also in order to also use these carbon system macromolecule component effectively, development of the manufacturing installation of fullerene which can separate a carbon system macromolecule component and fullerene as efficiently as possible, and the manufacture approach was desired.

[0010] Moreover, also in the manufacture approach of fullerene, the multi-annular aromatic compound generated with fullerene had become a problem. Although the soot-like matter containing two or more fullerene which is mainly concerned with C60 and C70 generates when manufacturing fullerene by the approach (combustion method) of carrying out the incomplete combustion of the organic substance, such as toluene, under the temperature and the flow and pressure requirement specifically controlled, it is known that 10 ppm - 5% of the weight of the multi-annular aromatic compound is contained in this soot-like matter (for example, refer to patent reference 3.).

[0011] Also in an aromatic compound, in presentation, as for this multi-annular aromatic compound, the appearance represented by the benzopyrene has few rates of a hydrogen atom, and it is similar to it with fullerene. Therefore, when intermingled in fullerene, the reactivity of fullerene may be checked, or the

property of the proper of fullerene may be affected. Moreover, a these multi-annular aromatic compound is poison, and it is necessary to reduce it as much as possible from the field of safety generally.

[0012] However, when the solubility to the solvent of fullerene and a multi-annular aromatic compound is measured, generally the solubility of a multi-annular aromatic compound is higher 10 or more times. If a solvent extracts the soot-like matter for the reason, it will be difficult to extract fullerene alternatively and it will extract most multi-annular aromatic compounds in the soot-like matter to coincidence to an extract. Even if for that reason it condenses and dries an extract, or it carries out solid content which condensed the extract and deposited a \*\* exception, dries and it obtains a solid-state (fullerene is mainly included) in order to obtain fullerene from this extract as a solid-state, the problem that about 0.01 - 10% of multi-annular aromatic compound will usually be contained is in this solid-state. This invention is made in view of a situation which was mentioned above, and it aims at offering the manufacturing installation and the manufacture approach of carrying out separation recovery of the fullerene efficiently from a lot of soot-like matter to generate in the case of extensive manufacture of fullerene.

[0013]

[Means for Solving the Problem] Generally, once a lot of existing carbon system macromolecule components in the soot-like matter become a solid-state, it is known to not changing to a gaseous state easily that fullerene will change to a gaseous state in a temperature field 400 degrees C or more.

[0014] The sublimation temperature of fullerene paid its attention to this invention persons that it is low temperature comparatively of 400 degrees C or more. And the soot-like matter was obtained as the condition which floated in the air current in the fullerene manufacture approach, and a specific combustion method and a specific thermal decomposition method specifically using the carbonaceous raw material, i.e., a soot-like matter content air current, and since this air current was usually the elevated temperature of existing extent, fullerene existed by the gaseous state, and I thought that a carbon system macromolecule component was in a solid state.

[0015] And as a result of this invention persons' inquiring wholeheartedly, from the soot-like matter content air current acquired by such specific approach, it found out that fullerene was separable from the soot-like matter containing the carbon system macromolecule component which also produces \*\* in large quantities in the manufacture process of fullerene not using an organic solvent and which is the so-called soot by the gaseous state. Furthermore, artificers found out that it was also disengageable at a gaseous state also in the serious harmful multi-annular aromatic compound contained in this soot-like matter. That is, since the sublimation temperature of this multi-annular aromatic compound is lower than that of fullerene The fullerene, the multi-annular aromatic compound which were obtained in the combustion method or the thermal decomposition method, And by heating the soot-like matter content air current containing a carbon system macromolecule component to the temperature which a multi-annular aromatic compound sublimates first, separating a multi-annular aromatic compound by the gaseous state, and subsequently heating a soot-like matter content air current further etc. A header and this invention were completed for fullerene being separable by the gaseous state.

[0016] That is, the summary of this invention consists in the manufacturing installation of the fullerene which has the decollator which separates the fullerene of a gaseous state, and/or the multi-annular aromatic compound of a gaseous state from the air current which contains fullerene, a multi-annular aromatic compound and the fullerene generation equipment that makes the air current containing the soot-like matter containing a carbon system macromolecule component generate, and the soot-like matter from a carbonaceous raw material.

[0017] Moreover, the unsatisfactory summary of this invention consists in the manufacture approach of the fullerene which has the following processes (1) and processes (2).

Process (1): The process which makes the soot-like matter content air current which contains fullerene, multi-annular aromatic compound fullerene, multi-annular aromatic hydrocarbon, and a carbon system macromolecule component by carrying out the incomplete combustion of the hydrocarbon raw material, or pyrolyzing a hydrocarbon raw material generate.

Process (2): The process which separates fullerene and/or a multi-annular aromatic compound from the

fullerene and the multi-annular aromatic compound which were obtained at the process (1), and the soot-like matter content air current containing a carbon system macromolecule component by the gaseous state.

[0018]

[Embodiment of the Invention] First, the manufacturing installation of fullerene is explained.

[0019] Drawing 1 is the whole example schematic diagram of the fullerene manufacturing installation concerning this invention at the time of using a combustion method in fullerene generation equipment. The fullerene manufacturing installation concerning this invention has the component of fullerene generation equipment 1, fullerene, and others, and the decollator 3 which specifically separates a multi-annular aromatic compound and a carbon system macromolecule component. It has preferably the deposit equipment 5 which deposits fullerene, and a decompression device 4 further. When using a combustion method for generation of fullerene, fullerene generation equipment 1 is generation equipment 1 which inert gas, such as helium, was made full and made the internal pressure reduced pressure conditions and the desirable condition near a vacuum to atmospheric pressure. Fullerene coal-for-coke-making-ized hydrogen, such as benzene introduced into the side face of this equipment from introductory tubing (not shown), is introduced in fullerene generation equipment 1 with oxygen. Moreover, in fullerene generation equipment 1, it has the burner 2 for making incomplete combustion cause coal-for-coke-making-ized hydrogen at least. The air current which contains the soot-like matter containing fullerene continuously according to such structure can be manufactured. By this invention, a lot of fullerene can be manufactured in succession by separating fullerene by the gaseous state from this soot-like matter content air current.

[0020] The decollator 3 of fullerene is installed in the interior or the lower stream of a river of fullerene generation equipment 1. Moreover, since what the inside of fullerene generation equipment 1 and a decollator 3 is generally made into the reduced pressure condition for is desirable in order to separate generation of fullerene, and fullerene by the gaseous state, it is desirable to have the decompression device 4 for decompressing the internal pressure of the generation equipment 1 of fullerene and a decollator 3. Although the soot-like matter content air current which contains fullerene from the generation equipment of fullerene flows with a decollator 3 and deposit equipment 5 in the manufacturing installation of the fullerene of this invention, since the flow of this air current is generally loose, in order to obtain fullerene efficiently, it is desirable to arrange a decompression device 4 following deposit equipment 5, and to pass an air current efficiently.

[0021] What has a well-known filter operation conventionally as a separation means to constitute a decollator 3 can be used. Usually, since generation of fullerene is performed under high temperature conditions, a heat-resistant filter is used as a filter used for the decollator 2 formed in the next of the generation equipment 1 of such fullerene. A heat-resistant filter is installed for the purpose for catching the soot component which exists as a solid-state at the temperature of 400 degrees C or more, and it is important for fullerene to install in the temperature field which sublimates and exists by the gaseous state. As such a filter, for example, the sintered metallic filter by the Japanese pole company, the sintered metallic filter by the Fuji filter company, etc. are mentioned. What is necessary is to choose the magnitude of a filter opening suitably and for the combustion conditions which make fullerene generate, and the description of the soot-like matter just to determine it. Since the sublimation temperature of fullerene changes also with degree of vacuums, it is important for it to install this filter in the location which can pass fullerene most efficiently with the degree of vacuum in a container.

[0022] As long as the quality of the material of this heat-resistant filter can bear an elevated temperature 300 degrees C or more, it may be anything, and a ceramic, a sintered metal, etc. are used suitably. Moreover, it is desirable that the carbon system macromolecule component by which uptake is carried out with this filter is equipped with the recovery means 6, such as back wash equipment discharged continuously. The carbon system giant-molecule component obtained in this phase is effectively utilizable as coloring agents, such as ink and a coating, the carbon black for tires, or a fuel. If the material which constitutes fullerene generation equipment 1 and \*\*\*\*\* 3 can bear above-mentioned temperature and a flow and pressure requirement, as the quality of the material, metals, such

as quartz glass and stainless steel, the ceramics, glass, etc. will be mentioned, for example.

[0023] Moreover, the thing of arbitration can be used for the separation approach in a decollator 3 for a batch type, a fixed-bed mold, a fluid bed mold, a continuation mold, etc. And in a decollator 3, inert gas may be further added in the air current introduced from fullerene generation equipment 1. What is necessary is to prepare the input and the exhaust port of inert gas in the decollator, and just to make inert gas flow and discharge continuously or intermittently in that case. Moreover, the temperature of the inert gas made to flow into a decollator 3 may be adjusted, and the temperature in a decollator 3 may be risen or dropped to predetermined temperature. Although this decollator 3 may separate fullerene and a multi-annular aromatic compound into coincidence by the gaseous state, the same decollator for separating a multi-annular aromatic compound as a decollator 3 may be formed in front of this decollator 3. Under the present circumstances, a multi-annular aromatic compound and fullerene become disengageable by the gaseous state separately.

[0024] The fullerene which passed the decollator 3 is the so-called "\*\*\*\* fullerene" containing the high order fullerene which has C60, C70, and the molecular weight beyond this. What is necessary is just to use the difference of such sublimation temperature, in order to generate this according to fullerene molecular weight further. Since sublimation temperature differs, fullerene, such as C60 and C70, can carry out separation uptake of C60 and C70 by installing an isolation region (not shown) in the location of temperature where each will be from a gaseous state in a solid state, respectively. As for such an isolation region that separates fullerene according to molecular weight, preparing in deposit equipment 5 is desirable. As an isolation region, the same filter as the decollator 3 of point \*\* and the temperature in the deposit field 5 may be lowered gradually, and each fullerene may make the internal surface of deposit equipment 5 etc. carry out a sequential deposit. Uptake of the fullerene can be carried out by installing a filter etc. in the location which finally becomes the temperature below the sublimation temperature of fullerene.

[0025] Then, the manufacture approach of the fullerene of this invention is described.

#### Process (1)

In the process (1) of this invention, the soot-like matter content air current containing fullerene is acquired. Under the present circumstances, fullerene is manufactured with the combustion method to which the incomplete combustion of the hydrocarbon (coal-for-coke-making-ized hydrogen) used as a raw material is carried out, or the thermal decomposition method which makes coal-for-coke-making-ized hydrogen decompose into the bottom of high temperature. Therefore, in the case of fullerene manufacture, since a multi-annular aromatic compound and a carbon system macromolecule component are also produced in coincidence, this soot-like matter content air current turns into an air current (soot-like matter content air current) containing fullerene, a multi-annular aromatic compound, and the soot-like matter containing a carbon system macromolecule component.

[0026] Since the temperature field where the maximum temperature in a fullerene composition region is low temperature comparatively compared with about 1700 degrees C and other approaches, and fullerene exists in the state of a gaseous phase, and carbon system macromolecule components other than fullerene which occupy many of soot-like matter especially exist in the state of a solid-state tends to specify a combustion method toward mass production method of fullerene and it can separate fullerene efficiently, it is desirable. What is necessary is it to be common to carry out under reduced pressure to atmospheric pressure as a flow and pressure requirement, and just to choose whenever [ reduced pressure ] suitably, when manufacturing fullerene with a combustion method. As a concrete flow and pressure requirement, 1330-13300Pa (10 - 100Torr) is desirable, and further 3990-6650Pa (30 - 50Torr) is desirable. Although what is necessary is just to choose suitably as temperature conditions according to the flow and pressure requirement which carried out point \*\*, 800-2500 degrees C is desirable especially, and it is especially desirable that it is 1200-1600 degrees C further 1000-2000 degrees C.

[0027] As a hydrocarbon used as the raw material of fullerene, the aromatic hydrocarbon of the carbon numbers 6-20, such as benzene, toluene, a xylene, naphthalene, a methylnaphthalene, an anthracene, and a phenanthrene, is used suitably. Moreover, as coal-for-coke-making-ized hydrogen, it may use together to these aromatic hydrocarbon, and aliphatic hydrocarbon, such as a hexane, a heptane, and an octane,

may be used.

[0028] The coal-for-coke-making-ized hydrogen used in a combustion method acts on coincidence also as a heat source. That is, it is thought that this coal-for-coke-making-ized hydrogen generates the carbon unit for forming a fullerene frame by carrying out the dehydrogenation of the coal-for-coke-making-ized hydrogen while raising the temperature which reacts with oxygen, generates heat and becomes generable [ fullerene ]. Carbon units gather on a fixed pressure and temperature conditions, and form fullerene.

[0029] Moreover, as for the ratio of a fuel required [ although what is necessary is just to also choose the rate of the fuel in combustion, and air suitably ] in order that an introductory air content may carry out stoichiometric combustion, and the fuel to throw in, in the volume ratio in ordinary temperature and ordinary pressure, it is usually desirable that it is 1:2-1:4, and further 1:2 to 1:2.5. As amount of the oxygen used in a combustion method, although it changes a little also with classes of coal-for-coke-making-ized hydrogen, when toluene is used, for example as coal-for-coke-making-ized hydrogen, a 0.5 to 9 time mol is desirable to toluene, and an one to 5 time mol is still more desirable. Inert gas may be made to exist in the system of reaction in a combustion method to fullerene in addition to oxygen. In this invention, inert gas means fullerene and the gas which does not react substantially. As a class of inert gas, helium, neon, an argon, nitrogen, and such mixture are mentioned.

[0030] In the soot-like matter obtained by the combustion method, fullerene and multi-annular aromatic hydrocarbon are contained. The remainders other than these are hydrocarbons, carbon black, etc. of a giant molecule which usually have some hydrogen atom by making carbon graphite structure with graphite structure into a frame (carbon system giant-molecule component). It is desirable that fullerene is contained in the soot-like matter obtained at a process (1) 5% of the weight or more, and especially the thing included especially 15% or more is desirable 10 more% or more. Moreover, although there will be no limit in a carbon number if the fullerene manufactured by this invention has fullerene structure, it is usually the fullerene of carbon numbers 60-84, and it is desirable that the percentage of C60 and C70 is 50% or more in [ all ] fullerene especially, and it is desirable that it is especially 80% or more 70 more% or more.

[0031] The soot-like matter content air current acquired at a process (1) has a loose rate, and usually has the temperature of 300 degrees C or more. This air current may be offered to the following process (2) as it is, the inert gas style of point \*\* is supplied, for example, an air speed may be raised, and the effectiveness in a process (2) may be raised, and this soot-like matter content air current may be heated if needed. Under the present circumstances, as for the temperature of a soot-like matter content air current, it is [ that what is necessary is just beyond the temperature in which fullerene and/or a multi-annular aromatic compound can exist with a gas ] desirable that it is specifically 400 degrees C or more. Moreover, when the temperature of a soot-like matter content air current is too high, the load to a fullerene manufacturing installation is large, and since the increment in the effectiveness of balancing a temperature rise decreases, it is desirable also in 2000 degrees C or less that it is 1500 degrees C or less. In addition, the multi-annular aromatic compound in this invention has at least one or more rings, and shows the aromatic compound which two or more rings have condensed. Naphthalene, an anthracene, a phenanthrene, a PENZO pyrene, etc. are mentioned as an example of a multi-annular aromatic compound.

[0032] (Process 2) A process (2) separates fullerene and/or a multi-annular aromatic compound from the soot-like matter content air current containing the fullerene, multi-annular aromatic compound, and carbon system macromolecule component which were obtained at the process (1) of point \*\* by the gaseous state. As a method of separation, the following (processes 2-1) and (a process 2-2) are mentioned.

(Process 2-1) A multi-annular aromatic compound is first separated from a soot-like matter content air current by the gaseous state. Next, the method of separating fullerene from the mixture of fullerene and a carbon system macromolecule component.

(Process 2-2) How to separate the multi-annular aromatic compound of the fullerene of a gaseous state, and a gaseous state first with other matter contained in soot-like matter, such as a carbon system macromolecule component, and then to separate fullerene from the mixture of fullerene and a multi-

annular aromatic compound. These processes are explained.

[0033] (Process 2-1) This process separates a multi-annular aromatic compound from a soot-like matter content air current by the gaseous state. What is necessary is to consider economical efficiency and just to carry out on the optimal conditions as separation conditions in this case, that what is necessary is just to choose the temperature of arbitration, and a flow and pressure requirement suitably, if a multi-annular aromatic compound can exist by the gaseous state. generally 100 to  $2 \times 10^5$  Pa of a pressure is desirable, and it is further 1000 to  $1.4 \times 10^5$  Pa -- it is desirable. In ordinary pressure, there is a merit to which equipment becomes easy, and since a multi-annular aromatic compound exists by the gaseous state even if separation condition temperature is low, it can dissociate, and there is an economical merit under reduced pressure.

[0034] Moreover, although separation condition temperature is based also on a pressure, it is 600 or less [ 100 degrees C or more ] preferably. What is necessary is just to choose separation condition temperature suitably, since the temperature in which a multi-annular aromatic compound can exist by the gaseous state naturally changes with pressures. When separation condition temperature is ordinary pressure, 200 more degrees C or more 600 degrees C or less are desirable, and 300 degrees C or more especially 550 degrees C or less are desirable. If temperature is too low, multi-annular aromatic hydrocarbon may deposit as a solid-state, since fullerene will also be in a gaseous state if temperature is too high conversely, it will dissociate with a multi-annular aromatic compound, and the recovery of fullerene may fall.

[0035] Although the soot-like matter content air current acquired at the process (1) may be used as it is on the occasion of separation of a multi-annular aromatic compound, inert gas like point \*\* may be added further. In order to avoid the reaction of these inert gas and fullerene, it is desirable for inert gas to permute the inside of a decollator substantially, and to separate a multi-annular aromatic compound under inert gas circulation. It is desirable to make the oxygen content in the gas in a decollator below 10 volume % especially, and also considering especially as one volume % is desirable below 5 volume %. If there are many oxygen contents, the oxide of fullerene may generate and the yield of fullerene may fall.

[0036] In the case of \*\*\*\*\* of a multi-annular aromatic compound, it is desirable that the sum total with the amount of inert gas carried in from a process (1) as an amount of circulation of inert gas to 1g of soot-like matter containing fullerene and multi-annular aromatic hydrocarbon is 1 - 10000 ml/min, and it is desirable that they are further 5 - 5000 ml/min. Circulation of inert gas may be continuous or may be intermittent. What is necessary is just to collect the multi-annular aromatic compounds separated with the decollator as a solid multi-annular aromatic compound by being accompanied to an air current, for example, lowering temperature with deposit equipment. This deposit equipment may be formed in the same equipment as a decollator, or may be formed as another equipment. Any of a batch type or continuous system are sufficient as recovery of this multi-annular aromatic compound. As it is, as a solid-state, it may dissolve in a solvent and recovery of the depositing multi-annular aromatic compound may be collected.

[0037] The technique of making it solidifying and collecting well-known gaseous state matter conventionally should just be used for a deposit of a multi-annular aromatic compound and the approach of recovery. For example, the gas which contains the multi-annular aromatic compound of a gaseous state in the cooled rotating drum is contacted, a multi-annular aromatic compound is deposited, and the approach of carrying out scraping recovery with a scraper intermittently or continuously is mentioned. moreover, it may dissolve with an organic solvent, and the multi-annular aromatic hydrocarbon which boiled the rotating drum and adhered may be removed and collected. moreover, gas is cooled by blowing the gas which is made to pass the multi-annular aromatic compound of a gaseous state through the spray zone of water or an organic solvent, or includes multi-annular aromatic series combination of a gaseous state as an option into water or an organic solvent, and the approach of carrying out deposit (or it dissolving in organic solvent -- making) recovery of the multi-annular aromatic compound is mentioned. Under the present circumstances, what is necessary is for an organic solvent just to extract a multi-annular aromatic compound further, when a multi-annular aromatic compound is deposited

underwater and collected underwater.

[0038] After separating a multi-annular aromatic compound at a process (2-1), fullerene is separated from the mixture of fullerene and a carbon system macromolecule component. Although especially a limit does not have a method of separating fullerene and a carbon system macromolecule component, the soot-like mixture which contains fullerene and a carbon system macromolecule component, for example mixes with an extracting solvent, and the approach (process 2-1-1) of obtaining the extract which fullerene dissolved, and the approach (process 2-1-2) of heating the soot-like mixture containing fullerene and a carbon system macromolecule component under existence of inert gas etc., and carrying out sublimation separation of the fullerene are mentioned.

[0039] (Process 2-1-1) The solvent which contains aromatic hydrocarbon preferably as an extracting solvent in the case of obtaining the extract which dissolved fullerene is used. As aromatic hydrocarbon, it is the hydrocarbon compound which has at least one benzene nucleus in intramolecular. Specifically Benzene, toluene, a xylene, ethylbenzene, n-propyl benzene, Isopropylbenzene, n-butylbenzene, sec-butylbenzene, tert-butylbenzene, 1 and 2, 3-trimethyl benzene, 1 and 2, 4-trimethyl benzene, Alkyl naphthalene, such as alkylbenzenes, such as 1,3,5-trimethylbenzene, 1, 2 and 3, 4-tetramethyl benzene, 1, 2 and 3, 5-tetramethyl benzene, diethylbenzene, and a cymene, and 1-methylnaphthalene, a tetralin, etc. are mentioned. 1, 2, 3-trimethyl benzene, 1 and 2, 4-trimethyl benzene, and a tetralin are [ among these ] desirable.

[0040] Further, independently or while these, two or more sorts other than the aromatic hydrocarbon mentioned above as an extracting solvent may be used for organic solvents, such as aliphatic hydrocarbon and chlorinated hydrocarbon, at a rate of arbitration. As aliphatic hydrocarbon, a ring type, a non-ring type, etc. can use the aliphatic hydrocarbon of arbitration. As an example of ring type aliphatic hydrocarbon, the thing of a monocycle type and a polycyclic type is mentioned, for example, a cyclopentane, a cyclohexane, cycloheptane, cyclooctane, etc. are mentioned by the monocycle formula. Moreover, the methylcyclopentane which is the derivative of monocycle type aliphatic hydrocarbon, an ethyl cyclopentane, a methylcyclohexane, ethylcyclohexane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, 1,4-dimethylcyclohexane, an isopropyl cyclohexane, n-propyl cyclohexane, t-butyl cyclohexane, n-butyl cyclohexane, an isobutyl cyclohexane, 1 and 2, a 4-trimethyl cyclohexane, 1 and 3, a 5-trimethyl cyclohexane, etc. are mentioned. A decalin etc. is mentioned as a polycyclic type. As an example of non-ring type aliphatic hydrocarbon, n pentane, n-hexane, n-heptane, n-octane, an isooctane, n-nonane, n-Deccan, n-dodecane, n tetradecane, etc. are mentioned.

[0041] As a chlorinated hydrocarbon, dichloromethane, chloroform, a carbon tetrachloride, a trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, a chlorobenzene, a dichlorobenzene, 1-chloronaphthalene, etc. are mentioned. In addition, a with a carbon numbers of six or more ketone, with a carbon numbers of six or more ester, with a carbon numbers of six or more ether, a carbon disulfide, etc. may be used.

[0042] Since the extraction efficiency of fullerene will fall if the solubility of the fullerene in an extracting solvent is too low, it is desirable that it is  $\geq 5$  g /l. ] or more as solubility of fullerene, and it is desirable that 10 more g /or more is [ 1. ] 15g/l. or more especially. Moreover, the boiling point is suitable for a 120-250-degree C thing also in 100-300 degrees C with the ordinary temperature liquid in a industrial viewpoint to these extracting solvents.

[0043] Only the amount which can fully extract fullerene needs to be used for an extracting solvent. Usually, when the amount of 5 - 400 weight double and economical efficiency are considered to the fullerene content in soot-like mixture, it is desirable to carry out the amount extent use of 40-200 weight double. Formats, such as a batch type, semi continuous system, continuous system, or those combination, and especially equipment are not limited for an extract. In addition, although 5 - 30% of the weight of fullerene is usually contained in soot-like mixture, since it is desirable to consider as the range which mentioned above the amount of the extracting solvent used to fullerene from a viewpoint of extraction efficiency, it is desirable to analyze some soot-like matter and to measure the fullerene content in the soot-like matter in advance of extract operation.

[0044] As an extractor, a churning mixing chamber can use it suitably. In the case of an extract, there is



no pressure in a container and it should just carry out especially a limit by ordinary pressure. As temperature at the time of an extract, it is usually -10-150 degrees C, is 5-80 degrees C preferably, and is 30-50 degrees C still more preferably. If it is these range, it is desirable from the field of the improvement in extraction efficiency, but since temperature dependence is small, as for extraction efficiency, it is advantageous to carry out with ordinary temperature extent in energy cost. In an extract process, if it extracts if needed further, irradiating a supersonic wave etc. at an extract, since extract time amount will become short, it is desirable.

[0045] In this way, since fullerene is dissolving in the obtained extract and the polynuclear aromatic compound is already removed at the front process (process (2-1)), the fullerene of a high grade can be obtained by distilling off the organic solvent used from the extract etc. in addition -- the slurry which remained after extracting fullerene -- the shape of an industry -- the useful carbon system macromolecule component is contained. Therefore, it is possible to carry out a non-melt a \*\* exception and to reuse it from this slurry. Although a \*\* exception is not limited, its pressure filtration is [ approaches, such as filtration under reduced pressure, pressure filtration, gravity filtration, filter filtration, or those combination, and especially equipment ] desirable especially.

[0046] (Process 2-1-2) The soot-like mixture containing fullerene and a carbon system macromolecule component with which the multi-annular aromatic compound was separated can separate fullerene from soot-like mixture by the gaseous state by giving under a high temperature service rather than the temperature at the time of separating a multi-annular aromatic compound by the gaseous state. Since fullerene generally serves as a solid-state after separating a multi-annular aromatic compound, by heating soot-like mixture, fullerene is sublimated and it can dissociate.

[0047] The conditions at the time of sublimating are carried out under ordinary pressure or reduced pressure of about 5000Pa. In ordinary pressure, there is a merit to which equipment becomes easy and there is a merit to which the sublimation temperature of fullerene becomes low under reduced pressure. What is necessary is to consider economical efficiency and just to carry out on the optimal conditions. The sum total with the amount of inert gas carried in from a front process to 1g of soot-like mixture in inert gas, such as nitrogen or helium, is 1 - 10000 ml/min. It is desirable extent and that it is 5 - 5000 ml/min extent preferably. Circulation of inert gas may be continuous or may be intermittent.

[0048] If a permutation is not fully carried out, the oxide of fullerene may generate. The preheating of the inert gas at the time of sublimating may be carried out, and it does not have to carry out a preheating. As for the equipment used for sublimation, a batch type, a fixed-bed mold, a fluid bed mold, a continuation mold, etc. do not carry out especially limitation. This process separates fullerene from the air current containing soot-like mixture or this by the gaseous state. What is necessary is to consider economical efficiency and just to carry out on the optimal conditions as separation conditions in this case, that what is necessary is just to choose the temperature of arbitration, and a flow and pressure requirement suitably, if fullerene can exist by the gaseous state. As for a pressure, generally, it is desirable to carry out under reduced pressure of about 5000Pa. In ordinary pressure, there is a merit to which equipment becomes easy, and since fullerene exists by the gaseous state even if separation condition temperature is low, it can dissociate, and there is an economical merit under reduced pressure.

[0049] Moreover, it is usually especially desirable [ temperature ], although separation condition temperature is based also on a pressure that it is 800 degrees C - 1100 degrees C further 600-1200 degrees C 400 degrees C - 1400 degrees C. What is necessary is just to choose separation condition temperature suitably, since the temperature in which fullerene can exist by the gaseous state naturally changes with pressures. Since fullerene will not be in a gaseous state enough if temperature is too low, if yield may fall and temperature is too high conversely, when becoming disadvantageous economically and slight oxygen exists, this oxygen may react with fullerene, and may become an oxide, and the yield of fullerene may fall.

[0050] (Process 2-2) Next, the fullerene of a gaseous state and the multi-annular aromatic compound of a gaseous state are separated with other matter contained in soot-like matter, such as a carbon system macromolecule component, and how to separate fullerene is explained from the mixture of fullerene and a multi-annular aromatic compound below. Fullerene and a multi-annular aromatic compound are



separable from this soot-like matter content air current by the gaseous state attaching the soot-like matter content air current which contains the fullerene and the multi-annular aromatic compound which were obtained at the process (1), and a carbon system macromolecule component at this process (2-2) under the condition of the process (2-1-2) of point \*\*. The separation conditions in this case are the same as the process (2-1-2) of point \*\*. Thus, generally the fullerene and the multi-annular aromatic compound of a gaseous state which were separated cool these, and make them the mixture of the shape of the shape of a solid-state, and a liquid. Subsequently, what is necessary is just to separate fullerene and a multi-annular aromatic compound by approach like the process (2-2-1) shown below, for example, a process (2-2-2), and a process (2-2-3).

[0051] Process (2-2-1)

The process which cools, uses as such shape of a solid-state and liquid mixture the fullerene and the multi-annular aromatic compound which were obtained by the gaseous state through a process (2-2), heats this mixture, and separates a multi-annular aromatic compound by the gaseous state.

Process (2-2-2)

The process which separates fullerene as a solid-state, cooling the fullerene and the multi-annular aromatic compound which were obtained by the gaseous state through the process (2-2), and making a multi-annular aromatic compound into a gaseous state.

Process (2-2-3)

The process which it cools, the fullerene and the multi-annular aromatic compound which were obtained by the gaseous state are used as such shape of a solid-state and liquid mixture through a process (2-2), and the solubility of fullerene extracts a multi-annular aromatic compound from this mixture with an organic solvent with the high solubility of a multi-annular aromatic compound low, and is separated.

Each [ these ] process is explained.

[0052] Process (2-2-1)

In a process (2-2-1), it cools and let the fullerene and the multi-annular aromatic compound (gas) which were obtained by the gaseous state be such shape of a solid-state and liquid mixture. And this mixture is heated and fullerene and a multi-annular aromatic compound are separated. As conditions for this separation, if fullerene and a multi-annular aromatic compound are separable by the gaseous state, the temperature of arbitration and a pressure can be taken. For example, what is necessary is just to separate fullerene and a multi-annular aromatic compound by the gaseous state under the same temperature as the time of separating a multi-annular aromatic compound from the soot-like matter content air current in the process (2-1) of point \*\* by the gaseous state, and a flow and pressure requirement. The temperature in this case and a flow and pressure requirement consider economical efficiency, and should just carry it out on the optimal conditions. Especially, it is desirable also in this process (2-2-1) to consider as the desirable range in the same temperature as the time of separating a multi-annular aromatic compound from the soot-like matter content air current in the process (2-1) of point \*\* by the gaseous state and a flow and pressure requirement.

[0053] Process (2-2-2)

In a process (2-2-2), it becomes liquid and fullerene cools the fullerene and the multi-annular aromatic compound (gas) which were obtained by the gaseous state even in the shape of a solid-state, and the condition that it is separable with the multi-annular aromatic compound of a gaseous state so that only a multi-annular aromatic compound may be in a gaseous state that is, and fullerene and a multi-annular aromatic compound are separated. as the conditions for this separation -- fullerene -- the shape of a solid-state -- or if it becomes liquid and a multi-annular aromatic compound can exist by the gaseous state, the temperature of arbitration and a pressure can be taken. for example, the bottom of the same temperature as the time of separating a multi-annular aromatic compound from the soot-like matter content air current in the process (2-1) of point \*\* by the gaseous state, and a flow and pressure requirement -- fullerene -- the shape of a solid-state -- or what is necessary is to suppose that it is liquid and just to separate a multi-annular aromatic compound The temperature in this case and a flow and pressure requirement consider economical efficiency, and should just carry it out on the optimal conditions. Especially, it is desirable also in this process (2-2-2) to consider as the desirable range in the

same temperature as the time of separating a multi-annular aromatic compound from the soot-like matter content air current in the process (2-1) of point \*\* by the gaseous state and a flow and pressure requirement.

[0054] Process (2-2-3)

It is the process at which the solubility of fullerene extracts a multi-annular aromatic compound from the shape of a solid-state containing fullerene and a multi-annular aromatic compound, and liquid mixture low at this process (2-2-3), using an organic solvent with the high solubility of a multi-annular aromatic compound as an extracting solvent. this extracting solvent, i.e., the mixed solvent which contains the amides of the carbon numbers 3-5 of the carbon numbers 2-5, such as a ketones; tetrahydrofuran of the carbon numbers 3-5, such as an alcohols; acetone of the carbon numbers 1-4 of a methanol, ethanol, propanol, ethylene glycol, a glycerol, etc. and a methyl ethyl ketone, diethylether, and dioxane, such as ether; N.N-dimethylformamide, and these as an example of a solvent (a poor solvent may be called hereafter) with the low solubility of fullerene, is mentioned. Alcohols are desirable, especially, a with a carbon number of three or less thing is desirable, and especially 2-propanol (isopropyl alcohol) is [ among these ] desirable.

[0055] As solubility of the fullerene C60 of these poor solvents, it is desirable that it is 1g/l. or less, and it is desirable that 100 moremg /or less is [ 1. ] especially 50 or less mg/L. Although it may be directly contacted into the shape of a solid-state of point \*\*, and liquid mixture, generally, a poor solvent dissolves in the organic solvent which the both sides of fullerene and a multi-annular aromatic compound show high solubility, once uses this mixture as a solution, adds a poor solvent to this and deposits fullerene.

[0056] As for the amount of the poor solvent used in this case, it is desirable that it is amount extent of 1 - 30 weight double to the amount of organic solvents used for this solution adjustment also in the amount of 0.1 - 50 weight double. If there are few amounts of a poor solvent, the amount of deposits of fullerene will decrease and recoverable fullerene will decrease. If many [ too ], the container capacity which performs these actuation will become large, and a loss will occur economically. As temperature which mixes a poor solvent, it is -20-150 degrees C, and it is usually desirable especially that it is 30-60 degrees C further 10-80 degrees C -10-100 degrees C. What is necessary is for filtration etc. just to recover the fullerene which deposited by mixing a poor solvent. On the other hand, since most multi-annular aromatic hydrocarbon is dissolved into a solvent, without depositing, the solution after removing fullerene can collect multi-annular aromatic compounds as a solid-state by distilling off the solvent etc.

[0057]

[Example] Although an example is shown below and this invention is explained to it still more concretely, unless the summary of this invention is exceeded, this invention is not limited to the following examples.

[0058]

[Example 1] 3.8mg of soot-like matter obtained by the combustion method by using toluene as a raw material was heated from the room temperature to 1150 degrees C in 20-degree-C per minute in desiccation nitrogen gas 100 cc/min using the apparatus for thermogravimetry ( TG-DTA6300 by SEIKO CORP.), and change of weight was measured. The obtained result is shown in drawing 2 . In drawing 2 , in a left axis of ordinate, a right axis of ordinate shows the rate of change of the rate of a raw material, and an axis of abscissa shows heating temperature for the rate of loss in quantity to the weight of 3.8mg. A passage clear from the graph which was shown in drawing 2 and which shows weight reduction, and the graph which shows weight rate of change, if temperature becomes 100 degrees C or more, weight will decrease gradually, and it turns out that weight reduction is accelerated from near 400 degree C. And in an elevated-temperature field 500 degrees C or more, the weight of the soot-like matter decreases rapidly. This is that a lot of fullerene in the soot-like matter will sublime if it takes into consideration that the sublimation temperature of fullerene is 400-800 degrees C, and it turns out that the rapid decrease of weight of the soot-like matter arose.

[0059] . Furthermore, qualitative analysis of the gas constituents generated when the soot-like matter was heated was performed on condition that the following using the quadrupole form mass spectroscope

(two to JEOL auto mass AM15 mold). A result is shown in drawing 3 .

A measuring method : The EI method furnace section temperature : 290 degrees C Transfer tube temperature : 285-degree-CGC oven temperature : 285-degree-C interface temperature : 285-degree-C ionization chamber temperature : 260-degree-C photograph mull electrical potential difference : 450V ionizing voltage : 70eV ionization current : 300microA mass range: 10 - 400amu scan speed : 1000msec [0060] In drawing 3 , an axis of ordinate shows the relative intensity of an ion spectrum, and an axis of abscissa shows heating temperature. From drawing 3 , the peak which shows existence of multi-annular aromatic compounds, such as aromatic compounds, such as benzene (molecular weight 78), toluene (molecular weight 92), and a xylene (molecular weight 106), and naphthalene (molecular weight 128), an anthracene (molecular weight 178), was checked in the temperature requirement lower than the sublimation temperature of fullerene in the gas which heated the soot-like matter and occurred. As for this, a multi-annular aromatic compound also shows that it is separable by the gaseous state as well as aromatic compounds, such as benzene. Fullerene and/or a multi-annular aromatic compound are separable from the fullerene and the multi-annular aromatic compound which were obtained by the combustion method, and the soot-like matter containing a carbon system macromolecule component by the gaseous state with the above example. Therefore, from the air current containing such soot-like matter, it is possible to separate fullerene and/or a multi-annular aromatic compound by the gaseous state continuously, and fullerene is continuously understood are disengageable from the air current containing this soot-like matter.

[0061]

[Effect of the Invention] According to this invention explained above, it becomes possible to be able to separate manufacture of fullerene, and fullerene and other soot components continuously within one equipment, and to produce a lot of fullerene continuously. When the fullerene which attracts attention since various as the exotic material which bears the next generation, and new materials is manufactured on a scale of industrial, a lot of soot-like matter and fullerene which are generated can be efficiently separated and collected to coincidence.

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[Translation done.]

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the manufacturing installation and the manufacture approach of the fullerene which is a new carbon material, and the fullerene which has the molecular structure of C60, C70, C76, C78, C82, and C84 especially.

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[Translation done.]

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**PRIOR ART**

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[Description of the Prior Art] The molecule-like carbon matter new type called the carbon cluster (spherical macromolecule) of the closed shell structured type of carbon numbers 60 and 70 and 84 grades is compounded, and attracts attention in 1990. The carbon cluster which has this special molecular structure is also called fullerene, and is called fullerene C60, this C70, this C84, etc. by the carbon number which constitutes that molecule frame (only called C60, C70, and C84 grade). These fullerene (it may only be hereafter called "fullerene") is new carbon materials, and since it is expected that unique physical properties will be shown from the special molecular structure, research on the property and application development is advanced briskly. As for fullerene, use in fields, such as for example, diamond coating, a cell ingredient, a coating, a heat insulator, lubricant, drugs, and cosmetics, is expected. In the field of (1) - (4) specifically shown below, innovative application development is being developed quickly.

[0003] (1) Application to a superhard ingredient : since purification of the artificial diamond which has a fine crystal grain child by using fullerene as a precursor is possible, use to an abrasion resistance material with added value is expected.

(2) Application to drugs : by using C60 derivative etc., research as an application of an anticancer agent, an acquired immunodeficiency syndrome, osteoporosis, the Alzheimer remedy, a contrast medium, a stent ingredient, etc. is advanced.

(3) Application to a superconducting material : if metallic potassium is doped to a fullerene thin film, it is discovered that a superconducting material with a high transition temperature called 18K can be made, and since various, attract attention.

(4) Application to semi-conductor manufacture : by mixing C60 with a photopolymer (resist), it uses that resist structure is strengthened further and the application to next-generation semi-conductor manufacture is expected.

[0004] It is the approach (arc discharge method) of evaporating a raw material by using as a raw material the electrode which consists of carbonaceous ingredients, such as (1) graphite, as the manufacture approach of fullerene, and making inter-electrode [ this ] producing arc discharge, (2) The approach (combustion method) of carrying out the incomplete combustion of the organic substance, such as a method (laser evaporation method) of evaporating a carbonaceous raw material and (4) benzene, by the pulse laser exposure of an approach (resistance heating method) and (3) high-energy consistency which a high current is passed [ exposure ] in a carbonaceous raw material, and evaporates a raw material etc. is learned.

[0005] however, the present condition -- two or more fullerene which cannot manufacture only the target single fullerene or fullerene of useful C60 - useful C84 grade, but is mainly concerned with C60 and C70 by any manufacture approach -- in addition, mixture (this products of combustion may be called the "soot-like matter") with many carbon compounds will be generated. Since it is about 10 - 30% also by the arc discharge method said for the content of the fullerene in this soot-like matter to be efficient, in order to obtain the fullerene of a high grade, it is necessary to separate fullerene from the soot-like matter.

[0006] As the separation approach of the fullerene from the soot-like matter, the solvent extraction method is known, for example. The carbon system giant-molecule component which occupies many of other soot-like matter to fullerene dissolving this in organic solvents, such as benzene, toluene, and a carbon disulfide, and which is the so-called "soot" is an approach using the property to be hard to dissolve in an organic solvent like graphite or amorphous carbon. Moreover, as an option which separates fullerene from the soot-like matter, the soot-like matter is heated under a high vacuum and the approach (the sublimating method) to which fullerene is made to sublime is learned. This sublimating method is the special separation approach which needs an elevated temperature 400 degrees C or more and the high vacuum conditions below 0.133Pa (10<sup>-3</sup>Torr), and since a solvent extraction method is easy to operate it compared with it, it is used widely. The fullerene furthermore obtained by the extract is a solution which mainly contains that of C60 and C70, and in order to separate single fullerene from this solution, the approach of carrying out clathration of the fullerene else [, such as column chromatography separation and judgment recrystallization, ] etc. is applied.

[0007] In addition, after carrying out contact processing of the solution which extracted the soot-like matter containing C60 with the organic solvent as the fullerene separation approach from the soot-like matter, and was obtained and which mainly contains C60 with activated carbon, there is a method of refining C60 by carrying out separation removal of the organic solvent from the obtained processing liquid (for example, refer to patent reference 1.). Moreover, as a separation refiner of fullerene, the separation refiner of the small quantity and batch type containing a heating container, a trap, and a decompression device is known. It specifically connects with the heating container and this heating container for making fullerene heat and sublime, and has a decompression device for carrying out reduced pressure suction of the interior of the trap for depositing the sublimated fullerene, and a heating container and a trap at least, and the heating container, the trap, and the decompression device are arranged in this sequence (for example, refer to patent reference 2.).

[0008]

[Patent reference 1] JP,5-85711,A [Patent reference 2] JP,9-227111,A [Patent reference 3] U.S. Pat. No. 5273729 specification

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] According to this invention explained above, it becomes possible to be able to separate manufacture of fullerene, and fullerene and other soot components continuously within one equipment, and to produce a lot of fullerene continuously. When the fullerene which attracts attention since various as the exotic material which bears the next generation, and new materials is manufactured on a scale of industrial, a lot of soot-like matter and fullerene which are generated can be efficiently separated and collected to coincidence.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, each of these separation purification approaches is batch types, and is the purification techniques for the little soot-like matter. Therefore, it is unsuitable for fullerene manufacture on the industrial scale which makes a lot of soot-like matter applicable to purification. Moreover, current [ which is represented by carbon black ], the carbon system macromolecule component which is worthy soot industrially are contained in this soot-like matter in large quantities. Therefore, from a lot of soot-like matter, also in order to also use these carbon system macromolecule component effectively, development of the manufacturing installation of fullerene which can separate a carbon system macromolecule component and fullerene as efficiently as possible, and the manufacture approach was desired.

[0010] Moreover, also in the manufacture approach of fullerene, the multi-annular aromatic compound generated with fullerene had become a problem. Although the soot-like matter containing two or more fullerene which is mainly concerned with C60 and C70 generates when manufacturing fullerene by the approach (combustion method) of carrying out the incomplete combustion of the organic substance, such as toluene, under the temperature and the flow and pressure requirement specifically controlled, it is known that 10 ppm - 5% of the weight of the multi-annular aromatic compound is contained in this soot-like matter (for example, refer to patent reference 3.).

[0011] Also in an aromatic compound, in presentation, as for this multi-annular aromatic compound, the appearance represented by the benzopyrene has few rates of a hydrogen atom, and it is similar to it with fullerene. Therefore, when intermingled in fullerene, the reactivity of fullerene may be checked, or the property of the proper of fullerene may be affected. Moreover, a these multi-annular aromatic compound is poison, and it is necessary to reduce it as much as possible from the field of safety generally.

[0012] However, when the solubility to the solvent of fullerene and a multi-annular aromatic compound is measured, generally the solubility of a multi-annular aromatic compound is higher 10 or more times. If a solvent extracts the soot-like matter for the reason, it will be difficult to extract fullerene alternatively and it will extract most multi-annular aromatic compounds in the soot-like matter to coincidence to an extract. Even if for that reason it condenses and dries an extract, or it carries out solid content which condensed the extract and deposited a \*\* exception, dries and it obtains a solid-state (fullerene is mainly included) in order to obtain fullerene from this extract as a solid-state, the problem that about 0.01 - 10% of multi-annular aromatic compound will usually be contained is in this solid-state. This invention is made in view of a situation which was mentioned above, and it aims at offering the manufacturing installation and the manufacture approach of carrying out separation recovery of the fullerene efficiently from a lot of soot-like matter to generate in the case of extensive manufacture of fullerene.

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**MEANS**

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[Means for Solving the Problem] Generally, once a lot of existing carbon system macromolecule components in the soot-like matter become a solid-state, it is known to not changing to a gaseous state easily that fullerene will change to a gaseous state in a temperature field 400 degrees C or more. [0014] The sublimation temperature of fullerene paid its attention to this invention persons that it is low temperature comparatively of 400 degrees C or more. And the soot-like matter was obtained as the condition which floated in the air current in the fullerene manufacture approach, and a specific combustion method and a specific thermal decomposition method specifically using the carbonaceous raw material, i.e., a soot-like matter content air current, and since this air current was usually the elevated temperature of existing extent, fullerene existed by the gaseous state, and I thought that a carbon system macromolecule component was in a solid state.

[0015] And as a result of this invention persons' inquiring wholeheartedly, from the soot-like matter content air current acquired by such specific approach, it found out that fullerene was separable from the soot-like matter containing the carbon system macromolecule component which also produces \*\* in large quantities in the manufacture process of fullerene not using an organic solvent and which is the so-called soot by the gaseous state. Furthermore, artificers found out that it was also disengageable at a gaseous state also in the serious harmful multi-annular aromatic compound contained in this soot-like matter. That is, since the sublimation temperature of this multi-annular aromatic compound is lower than that of fullerene The fullerene, the multi-annular aromatic compound which were obtained in the combustion method or the thermal decomposition method, And by heating the soot-like matter content air current containing a carbon system macromolecule component to the temperature which a multi-annular aromatic compound sublimates first, separating a multi-annular aromatic compound by the gaseous state, and subsequently heating a soot-like matter content air current further etc. A header and this invention were completed for fullerene being separable by the gaseous state.

[0016] That is, the summary of this invention consists in the manufacturing installation of the fullerene which has the decollator which separates the fullerene of a gaseous state, and/or the multi-annular aromatic compound of a gaseous state from the air current which contains fullerene, a multi-annular aromatic compound and the fullerene generation equipment that makes the air current containing the soot-like matter containing a carbon system macromolecule component generate, and the soot-like matter from a carbonaceous raw material.

[0017] Moreover, the unsatisfactory summary of this invention consists in the manufacture approach of the fullerene which has the following processes (1) and processes (2).

Process (1): The process which makes the soot-like matter content air current which contains fullerene, multi-annular aromatic compound fullerene, multi-annular aromatic hydrocarbon, and a carbon system macromolecule component by carrying out the incomplete combustion of the hydrocarbon raw material, or pyrolyzing a hydrocarbon raw material generate.

Process (2): The process which separates fullerene and/or a multi-annular aromatic compound from the fullerene and the multi-annular aromatic compound which were obtained at the process (1), and the soot-like matter content air current containing a carbon system macromolecule component by the gaseous

state.

[0018]

[Embodiment of the Invention] First, the manufacturing installation of fullerene is explained.

[0019] Drawing 1 is the whole example schematic diagram of the fullerene manufacturing installation concerning this invention at the time of using a combustion method in fullerene generation equipment. The fullerene manufacturing installation concerning this invention has the component of fullerene generation equipment 1, fullerene, and others, and the decollator 3 which specifically separates a multi-annular aromatic compound and a carbon system macromolecule component. It has preferably the deposit equipment 5 which deposits fullerene, and a decompression device 4 further. When using a combustion method for generation of fullerene, fullerene generation equipment 1 is generation equipment 1 which inert gas, such as helium, was made full and made the internal pressure reduced pressure conditions and the desirable condition near a vacuum to atmospheric pressure. Fullerene coal-for-coke-making-ized hydrogen, such as benzene introduced into the side face of this equipment from introductory tubing (not shown), is introduced in fullerene generation equipment 1 with oxygen. Moreover, in fullerene generation equipment 1, it has the burner 2 for making incomplete combustion cause coal-for-coke-making-ized hydrogen at least. The air current which contains the soot-like matter containing fullerene continuously according to such structure can be manufactured. By this invention, a lot of fullerene can be manufactured in succession by separating fullerene by the gaseous state from this soot-like matter content air current.

[0020] The decollator 3 of fullerene is installed in the interior or the lower stream of a river of fullerene generation equipment 1. Moreover, since what the inside of fullerene generation equipment 1 and a decollator 3 is generally made into the reduced pressure condition for is desirable in order to separate generation of fullerene, and fullerene by the gaseous state, it is desirable to have the decompression device 4 for decompressing the internal pressure of the generation equipment 1 of fullerene and a decollator 3. Although the soot-like matter content air current which contains fullerene from the generation equipment of fullerene flows with a decollator 3 and deposit equipment 5 in the manufacturing installation of the fullerene of this invention, since the flow of this air current is generally loose, in order to obtain fullerene efficiently, it is desirable to arrange a decompression device 4 following deposit equipment 5, and to pass an air current efficiently.

[0021] What has a well-known filter operation conventionally as a separation means to constitute a decollator 3 can be used. Usually, since generation of fullerene is performed under high temperature conditions, a heat-resistant filter is used as a filter used for the decollator 2 formed in the next of the generation equipment 1 of such fullerene. A heat-resistant filter is installed for the purpose for catching the soot component which exists as a solid-state at the temperature of 400 degrees C or more, and it is important for fullerene to install in the temperature field which sublimates and exists by the gaseous state. As such a filter, for example, the sintered metallic filter by the Japanese pole company, the sintered metallic filter by the Fuji filter company, etc. are mentioned. What is necessary is to choose the magnitude of a filter opening suitably and for the combustion conditions which make fullerene generate, and the description of the soot-like matter just to determine it. Since the sublimation temperature of fullerene changes also with degree of vacuums, it is important for it to install this filter in the location which can pass fullerene most efficiently with the degree of vacuum in a container.

[0022] As long as the quality of the material of this heat-resistant filter can bear an elevated temperature 300 degrees C or more, it may be anything, and a ceramic, a sintered metal, etc. are used suitably. Moreover, it is desirable that the carbon system macromolecule component by which uptake is carried out with this filter is equipped with the recovery means 6, such as back wash equipment discharged continuously. The carbon system giant-molecule component obtained in this phase is effectively utilizable as coloring agents, such as ink and a coating, the carbon black for tires, or a fuel. If the material which constitutes fullerene generation equipment 1 and \*\*\*\*\* 3 can bear above-mentioned temperature and a flow and pressure requirement, as the quality of the material, metals, such as quartz glass and stainless steel, the ceramics, glass, etc. will be mentioned, for example.

[0023] Moreover, the thing of arbitration can be used for the separation approach in a decollator 3 for a

batch type, a fixed-bed mold, a fluid bed mold, a continuation mold, etc. And in a decollator 3, inert gas may be further added in the air current introduced from fullerene generation equipment 1. What is necessary is to prepare the input and the exhaust port of inert gas in the decollator, and just to make inert gas flow and discharge continuously or intermittently in that case. Moreover, the temperature of the inert gas made to flow into a decollator 3 may be adjusted, and the temperature in a decollator 3 may be risen or dropped to predetermined temperature. Although this decollator 3 may separate fullerene and a multi-annular aromatic compound into coincidence by the gaseous state, the same decollator for separating a multi-annular aromatic compound as a decollator 3 may be formed in front of this decollator 3. Under the present circumstances, a multi-annular aromatic compound and fullerene become disengageable by the gaseous state separately.

[0024] The fullerene which passed the decollator 3 is the so-called "\*\*\*\* fullerene" containing the high order fullerene which has C60, C70, and the molecular weight beyond this. What is necessary is just to use the difference of such sublimation temperature, in order to generate this according to fullerene molecular weight further. Since sublimation temperature differs, fullerene, such as C60 and C70, can carry out separation uptake of C60 and C70 by installing an isolation region (not shown) in the location of temperature where each will be from a gaseous state in a solid state, respectively. As for such an isolation region that separates fullerene according to molecular weight, preparing in deposit equipment 5 is desirable. As an isolation region, the same filter as the decollator 3 of point \*\* and the temperature in the deposit field 5 may be lowered gradually, and each fullerene may make the internal surface of deposit equipment 5 etc. carry out a sequential deposit. Uptake of the fullerene can be carried out by installing a filter etc. in the location which finally becomes the temperature below the sublimation temperature of fullerene.

[0025] Then, the manufacture approach of the fullerene of this invention is described.

#### Process (1)

In the process (1) of this invention, the soot-like matter content air current containing fullerene is acquired. Under the present circumstances, fullerene is manufactured with the combustion method to which the incomplete combustion of the hydrocarbon (coal-for-coke-making-ized hydrogen) used as a raw material is carried out, or the thermal decomposition method which makes coal-for-coke-making-ized hydrogen decompose into the bottom of high temperature. Therefore, in the case of fullerene manufacture, since a multi-annular aromatic compound and a carbon system macromolecule component are also produced in coincidence, this soot-like matter content air current turns into an air current (soot-like matter content air current) containing fullerene, a multi-annular aromatic compound, and the soot-like matter containing a carbon system macromolecule component.

[0026] Since the temperature field where the maximum temperature in a fullerene composition region is low temperature comparatively compared with about 1700 degrees C and other approaches, and fullerene exists in the state of a gaseous phase, and carbon system macromolecule components other than fullerene which occupy many of soot-like matter especially exist in the state of a solid-state tends to specify a combustion method toward mass production method of fullerene and it can separate fullerene efficiently, it is desirable. What is necessary is it to be common to carry out under reduced pressure to atmospheric pressure as a flow and pressure requirement, and just to choose whenever [ reduced pressure ] suitably, when manufacturing fullerene with a combustion method. As a concrete flow and pressure requirement, 1330-13300Pa (10 - 100Torr) is desirable, and further 3990-6650Pa (30 - 50Torr) is desirable. Although what is necessary is just to choose suitably as temperature conditions according to the flow and pressure requirement which carried out point \*\*, 800-2500 degrees C is desirable especially, and it is especially desirable that it is 1200-1600 degrees C further 1000-2000 degrees C.

[0027] As a hydrocarbon used as the raw material of fullerene, the aromatic hydrocarbon of the carbon numbers 6-20, such as benzene, toluene, a xylene, naphthalene, a methylnaphthalene, an anthracene, and a phenanthrene, is used suitably. Moreover, as coal-for-coke-making-ized hydrogen, it may use together to these aromatic hydrocarbon, and aliphatic hydrocarbon, such as a hexane, a heptane, and an octane, may be used.

[0028] The coal-for-coke-making-ized hydrogen used in a combustion method acts on coincidence also

as a heat source. That is, it is thought that this coal-for-coke-making-ized hydrogen generates the carbon unit for forming a fullerene frame by carrying out the dehydrogenation of the coal-for-coke-making-ized hydrogen while raising the temperature which reacts with oxygen, generates heat and becomes generable [ fullerene ]. Carbon units gather on a fixed pressure and temperature conditions, and form fullerene.

[0029] Moreover, as for the ratio of a fuel required [ although what is necessary is just to also choose the rate of the fuel in combustion, and air suitably ] in order that an introductory air content may carry out stoichiometric combustion, and the fuel to throw in, in the volume ratio in ordinary temperature and ordinary pressure, it is usually desirable that it is 1:2-1:4, and further 1:2 to 1:2.5. As amount of the oxygen used used in a combustion method, although it changes a little also with classes of coal-for-coke-making-ized hydrogen, when toluene is used, for example as coal-for-coke-making-ized hydrogen, a 0.5 to 9 time mol is desirable to toluene, and an one to 5 time mol is still more desirable. Inert gas may be made to exist in the system of reaction in a combustion method to fullerene in addition to oxygen. In this invention, inert gas means fullerene and the gas which does not react substantially. As a class of inert gas, helium, neon, an argon, nitrogen, and such mixture are mentioned.

[0030] In the soot-like matter obtained by the combustion method, fullerene and multi-annular aromatic hydrocarbon are contained. The remainders other than these are hydrocarbons, carbon black, etc. of a giant molecule which usually have some hydrogen atom by making carbon graphite structure with graphite structure into a frame (carbon system giant-molecule component). It is desirable that fullerene is contained in the soot-like matter obtained at a process (1) 5% of the weight or more, and especially the thing included especially 15% or more is desirable 10 more% or more. Moreover, although there will be no limit in a carbon number if the fullerene manufactured by this invention has fullerene structure, it is usually the fullerene of carbon numbers 60-84, and it is desirable that the percentage of C60 and C70 is 50% or more in [ all ] fullerene especially, and it is desirable that it is especially 80% or more 70 more% or more.

[0031] The soot-like matter content air current acquired at a process (1) has a loose rate, and usually has the temperature of 300 degrees C or more. This air current may be offered to the following process (2) as it is, the inert gas style of point \*\* is supplied, for example, an air speed may be raised, and the effectiveness in a process (2) may be raised, and this soot-like matter content air current may be heated if needed. Under the present circumstances, as for the temperature of a soot-like matter content air current, it is [ that what is necessary is just beyond the temperature in which fullerene and/or a multi-annular aromatic compound can exist with a gas ] desirable that it is specifically 400 degrees C or more. Moreover, when the temperature of a soot-like matter content air current is too high, the load to a fullerene manufacturing installation is large, and since the increment in the effectiveness of balancing a temperature rise decreases, it is desirable also in 2000 degrees C or less that it is 1500 degrees C or less. In addition, the multi-annular aromatic compound in this invention has at least one or more rings, and shows the aromatic compound which two or more rings have condensed. Naphthalene, an anthracene, a phenanthrene, a PENZO pyrene, etc. are mentioned as an example of a multi-annular aromatic compound.

[0032] (Process 2) A process (2) separates fullerene and/or a multi-annular aromatic compound from the soot-like matter content air current containing the fullerene, multi-annular aromatic compound, and carbon system macromolecule component which were obtained at the process (1) of point \*\* by the gaseous state. As a method of separation, the following (processes 2-1) and (a process 2-2) are mentioned.

(Process 2-1) A multi-annular aromatic compound is first separated from a soot-like matter content air current by the gaseous state. Next, the method of separating fullerene from the mixture of fullerene and a carbon system macromolecule component.

(Process 2-2) How to separate the multi-annular aromatic compound of the fullerene of a gaseous state, and a gaseous state first with other matter contained in soot-like matter, such as a carbon system macromolecule component, and then to separate fullerene from the mixture of fullerene and a multi-annular aromatic compound. These processes are explained.

[0033] (Process 2-1) This process separates a multi-annular aromatic compound from a soot-like matter

content air current by the gaseous state. What is necessary is to consider economical efficiency and just to carry out on the optimal conditions as separation conditions in this case, that what is necessary is just to choose the temperature of arbitration, and a flow and pressure requirement suitably, if a multi-annular aromatic compound can exist by the gaseous state. generally 100 to  $2 \times 10^5$  Pa of a pressure is desirable, and it is further 1000 to  $1.4 \times 10^5$  Pa -- it is desirable. In ordinary pressure, there is a merit to which equipment becomes easy, and since a multi-annular aromatic compound exists by the gaseous state even if separation condition temperature is low, it can dissociate, and there is an economical merit under reduced pressure.

[0034] Moreover, although separation condition temperature is based also on a pressure, it is 600 or less [ 100 degrees C or more ] preferably. What is necessary is just to choose separation condition temperature suitably, since the temperature in which a multi-annular aromatic compound can exist by the gaseous state naturally changes with pressures. When separation condition temperature is ordinary pressure, 200 more degrees C or more 600 degrees C or less are desirable, and 300 degrees C or more especially 550 degrees C or less are desirable. If temperature is too low, multi-annular aromatic hydrocarbon may deposit as a solid-state, since fullerene will also be in a gaseous state if temperature is too high conversely, it will dissociate with a multi-annular aromatic compound, and the recovery of fullerene may fall.

[0035] Although the soot-like matter content air current acquired at the process (1) may be used as it is on the occasion of separation of a multi-annular aromatic compound, inert gas like point \*\* may be added further. In order to avoid the reaction of these inert gas and fullerene, it is desirable for inert gas to permute the inside of a decollator substantially, and to separate a multi-annular aromatic compound under inert gas circulation. It is desirable to make the oxygen content in the gas in a decollator below 10 volume % especially, and also considering especially as one volume % is desirable below 5 volume %. If there are many oxygen contents, the oxide of fullerene may generate and the yield of fullerene may fall.

[0036] In the case of \*\*\*\*\* of a multi-annular aromatic compound, it is desirable that the sum total with the amount of inert gas carried in from a process (1) as an amount of circulation of inert gas to 1g of soot-like matter containing fullerene and multi-annular aromatic hydrocarbon is 1 - 10000 ml/min, and it is desirable that they are further 5 - 5000 ml/min. Circulation of inert gas may be continuous or may be intermittent. What is necessary is just to collect the multi-annular aromatic compounds separated with the decollator as a solid multi-annular aromatic compound by being accompanied to an air current, for example, lowering temperature with deposit equipment. This deposit equipment may be formed in the same equipment as a decollator, or may be formed as another equipment. Any of a batch type or continuous system are sufficient as recovery of this multi-annular aromatic compound. As it is, as a solid-state, it may dissolve in a solvent and recovery of the depositing multi-annular aromatic compound may be collected.

[0037] The technique of making it solidifying and collecting well-known gaseous state matter conventionally should just be used for a deposit of a multi-annular aromatic compound and the approach of recovery. For example, the gas which contains the multi-annular aromatic compound of a gaseous state in the cooled rotating drum is contacted, a multi-annular aromatic compound is deposited, and the approach of carrying out scraping recovery with a scraper intermittently or continuously is mentioned. moreover, it may dissolve with an organic solvent, and the multi-annular aromatic hydrocarbon which boiled the rotating drum and adhered may be removed and collected. moreover, gas is cooled by blowing the gas which is made to pass the multi-annular aromatic compound of a gaseous state through the spray zone of water or an organic solvent, or includes multi-annular aromatic series combination of a gaseous state as an option into water or an organic solvent, and the approach of carrying out deposit (or it dissolving in organic solvent -- making) recovery of the multi-annular aromatic compound is mentioned. Under the present circumstances, what is necessary is for an organic solvent just to extract a multi-annular aromatic compound further, when a multi-annular aromatic compound is deposited underwater and collected underwater.

[0038] After separating a multi-annular aromatic compound at a process (2-1), fullerene is separated

from the mixture of fullerene and a carbon system macromolecule component. Although especially a limit does not have a method of separating fullerene and a carbon system macromolecule component, the soot-like mixture which contains fullerene and a carbon system macromolecule component, for example mixes with an extracting solvent, and the approach (process 2-1-1) of obtaining the extract which fullerene dissolved, and the approach (process 2-1-2) of heating the soot-like mixture containing fullerene and a carbon system macromolecule component under existence of inert gas etc., and carrying out sublimation separation of the fullerene are mentioned.

[0039] (Process 2-1-1) The solvent which contains aromatic hydrocarbon preferably as an extracting solvent in the case of obtaining the extract which dissolved fullerene is used. As aromatic hydrocarbon, it is the hydrocarbon compound which has at least one benzene nucleus in intramolecular. Specifically Benzene, toluene, a xylene, ethylbenzene, n-propyl benzene, Isopropylbenzene, n-butylbenzene, sec-butylbenzene, tert-butylbenzene, 1 and 2, 3-trimethyl benzene, 1 and 2, 4-trimethyl benzene, Alkyl naphthalene, such as alkylbenzenes, such as 1,3,5-trimethylbenzene, 1, 2 and 3, 4-tetramethyl benzene, 1, 2 and 3, 5-tetramethyl benzene, diethylbenzene, and a cymene, and 1-methylnaphthalene, a tetralin, etc. are mentioned. 1, 2, 3-trimethyl benzene, 1 and 2, 4-trimethyl benzene, and a tetralin are [ among these ] desirable.

[0040] Further, independently or while these, two or more sorts other than the aromatic hydrocarbon mentioned above as an extracting solvent may be used for organic solvents, such as aliphatic hydrocarbon and chlorinated hydrocarbon, at a rate of arbitration. As aliphatic hydrocarbon, a ring type, a non-ring type, etc. can use the aliphatic hydrocarbon of arbitration. As an example of ring type aliphatic hydrocarbon, the thing of a monocycle type and a polycyclic type is mentioned, for example, a cyclopentane, a cyclohexane, cycloheptane, cyclooctane, etc. are mentioned by the monocycle formula. Moreover, the methylcyclopentane which is the derivative of monocycle type aliphatic hydrocarbon, an ethyl cyclopentane, a methylcyclohexane, ethylcyclohexane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, 1,4-dimethylcyclohexane, an isopropyl cyclohexane, n-propyl cyclohexane, t-butyl cyclohexane, n-butyl cyclohexane, an isobutyl cyclohexane, 1 and 2, a 4-trimethyl cyclohexane, 1 and 3, a 5-trimethyl cyclohexane, etc. are mentioned. A decalin etc. is mentioned as a polycyclic type. As an example of non-ring type aliphatic hydrocarbon, n pentane, n-hexane, n-heptane, n-octane, an isooctane, n-nonane, n-Deccan, n-dodecane, n tetradecane, etc. are mentioned.

[0041] As a chlorinated hydrocarbon, dichloromethane, chloroform, a carbon tetrachloride, a trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, a chlorobenzene, a dichlorobenzene, 1-chloronaphthalene, etc. are mentioned. In addition, a with a carbon numbers of six or more ketone, with a carbon numbers of six or more ester, with a carbon numbers of six or more ether, a carbon disulfide, etc. may be used.

[0042] Since the extraction efficiency of fullerene will fall if the solubility of the fullerene in an extracting solvent is too low, it is desirable that it is  $\geq 5$  g [l. ] or more as solubility of fullerene, and it is desirable that 10 moreg /or more is [ l. ] 15g/l. or more especially. Moreover, the boiling point is suitable for a 120-250-degree C thing also in 100-300 degrees C with the ordinary temperature liquid in a industrial viewpoint to these extracting solvents.

[0043] Only the amount which can fully extract fullerene needs to be used for an extracting solvent. Usually, when the amount of 5 - 400 weight double and economical efficiency are considered to the fullerene content in soot-like mixture, it is desirable to carry out the amount extent use of 40-200 weight double. Formats, such as a batch type, semi continuous system, continuous system, or those combination, and especially equipment are not limited for an extract. In addition, although 5 - 30% of the weight of fullerene is usually contained in soot-like mixture, since it is desirable to consider as the range which mentioned above the amount of the extracting solvent used to fullerene from a viewpoint of extraction efficiency, it is desirable to analyze some soot-like matter and to measure the fullerene content in the soot-like matter in advance of extract operation.

[0044] As an extractor, a churning mixing chamber can use it suitably. In the case of an extract, there is no pressure in a container and it should just carry out especially a limit by ordinary pressure. As temperature at the time of an extract, it is usually -10-150 degrees C, is 5-80 degrees C preferably, and is



30-50 degrees C still more preferably. If it is these range, it is desirable from the field of the improvement in extraction efficiency, but since temperature dependence is small, as for extraction efficiency, it is advantageous to carry out with ordinary temperature extent in energy cost. In an extract process, if it extracts if needed further, irradiating a supersonic wave etc. at an extract, since extract time amount will become short, it is desirable.

[0045] In this way, since fullerene is dissolving in the obtained extract and the polynuclear aromatic compound is already removed at the front process (process (2-1)), the fullerene of a high grade can be obtained by distilling off the organic solvent used from the extract etc. in addition -- the slurry which remained after extracting fullerene -- the shape of an industry -- the useful carbon system macromolecule component is contained. Therefore, it is possible to carry out a non-melt a \*\* exception and to reuse it from this slurry. Although a \*\* exception is not limited, its pressure filtration is [ approaches, such as filtration under reduced pressure, pressure filtration, gravity filtration, filter filtration, or those combination, and especially equipment ] desirable especially.

[0046] (Process 2-1-2) The soot-like mixture containing fullerene and a carbon system macromolecule component with which the multi-annular aromatic compound was separated can separate fullerene from soot-like mixture by the gaseous state by giving under a high temperature service rather than the temperature at the time of separating a multi-annular aromatic compound by the gaseous state. Since fullerene generally serves as a solid-state after separating a multi-annular aromatic compound, by heating soot-like mixture, fullerene is sublimated and it can dissociate.

[0047] The conditions at the time of sublimating are carried out under ordinary pressure or reduced pressure of about 5000Pa. In ordinary pressure, there is a merit to which equipment becomes easy and there is a merit to which the sublimation temperature of fullerene becomes low under reduced pressure. What is necessary is to consider economical efficiency and just to carry out on the optimal conditions. The sum total with the amount of inert gas carried in from a front process to 1g of soot-like mixture in inert gas, such as nitrogen or helium, is 1 - 10000 ml/min. It is desirable extent and that it is 5 - 5000 ml/min extent preferably. Circulation of inert gas may be continuous or may be intermittent.

[0048] If a permutation is not fully carried out, the oxide of fullerene may generate. The preheating of the inert gas at the time of sublimating may be carried out, and it does not have to carry out a preheating. As for the equipment used for sublimation, a batch type, a fixed-bed mold, a fluid bed mold, a continuation mold, etc. do not carry out especially limitation. This process separates fullerene from the air current containing soot-like mixture or this by the gaseous state. What is necessary is to consider economical efficiency and just to carry out on the optimal conditions as separation conditions in this case, that what is necessary is just to choose the temperature of arbitration, and a flow and pressure requirement suitably, if fullerene can exist by the gaseous state. As for a pressure, generally, it is desirable to carry out under reduced pressure of about 5000Pa. In ordinary pressure, there is a merit to which equipment becomes easy, and since fullerene exists by the gaseous state even if separation condition temperature is low, it can dissociate, and there is an economical merit under reduced pressure.

[0049] Moreover, it is usually especially desirable [ temperature ], although separation condition temperature is based also on a pressure that it is 800 degrees C - 1100 degrees C further 600-1200 degrees C 400 degrees C - 1400 degrees C. What is necessary is just to choose separation condition temperature suitably, since the temperature in which fullerene can exist by the gaseous state naturally changes with pressures. Since fullerene will not be in a gaseous state enough if temperature is too low, if yield may fall and temperature is too high conversely, when becoming disadvantageous economically and slight oxygen exists, this oxygen may react with fullerene, and may become an oxide, and the yield of fullerene may fall.

[0050] (Process 2-2) Next, the fullerene of a gaseous state and the multi-annular aromatic compound of a gaseous state are separated with other matter contained in soot-like matter, such as a carbon system macromolecule component, and how to separate fullerene is explained from the mixture of fullerene and a multi-annular aromatic compound below. Fullerene and a multi-annular aromatic compound are separable from this soot-like matter content air current by the gaseous state attaching the soot-like matter content air current which contains the fullerene and the multi-annular aromatic compound which were



obtained at the process (1), and a carbon system macromolecule component at this process (2-2) under the condition of the process (2-1-2) of point \*\*. The separation conditions in this case are the same as the process (2-1-2) of point \*\*. Thus, generally the fullerene and the multi-annular aromatic compound of a gaseous state which were separated cool these, and make them the mixture of the shape of the shape of a solid-state, and a liquid. Subsequently, what is necessary is just to separate fullerene and a multi-annular aromatic compound by approach like the process (2-2-1) shown below, for example, a process (2-2-2), and a process (2-2-3).

[0051] Process (2-2-1)

The process which cools, uses as such shape of a solid-state and liquid mixture the fullerene and the multi-annular aromatic compound which were obtained by the gaseous state through a process (2-2), heats this mixture, and separates a multi-annular aromatic compound by the gaseous state.

Process (2-2-2)

The process which separates fullerene as a solid-state, cooling the fullerene and the multi-annular aromatic compound which were obtained by the gaseous state through the process (2-2), and making a multi-annular aromatic compound into a gaseous state.

Process (2-2-3)

The process which it cools, the fullerene and the multi-annular aromatic compound which were obtained by the gaseous state are used as such shape of a solid-state and liquid mixture through a process (2-2), and the solubility of fullerene extracts a multi-annular aromatic compound from this mixture with an organic solvent with the high solubility of a multi-annular aromatic compound low, and is separated. Each [ these ] process is explained.

[0052] Process (2-2-1)

In a process (2-2-1), it cools and let the fullerene and the multi-annular aromatic compound (gas) which were obtained by the gaseous state be such shape of a solid-state and liquid mixture. And this mixture is heated and fullerene and a multi-annular aromatic compound are separated. As conditions for this separation, if fullerene and a multi-annular aromatic compound are separable by the gaseous state, the temperature of arbitration and a pressure can be taken. For example, what is necessary is just to separate fullerene and a multi-annular aromatic compound by the gaseous state under the same temperature as the time of separating a multi-annular aromatic compound from the soot-like matter content air current in the process (2-1) of point \*\* by the gaseous state, and a flow and pressure requirement. The temperature in this case and a flow and pressure requirement consider economical efficiency, and should just carry it out on the optimal conditions. Especially, it is desirable also in this process (2-2-1) to consider as the desirable range in the same temperature as the time of separating a multi-annular aromatic compound from the soot-like matter content air current in the process (2-1) of point \*\* by the gaseous state and a flow and pressure requirement.

[0053] Process (2-2-2)

In a process (2-2-2), it becomes liquid and fullerene cools the fullerene and the multi-annular aromatic compound (gas) which were obtained by the gaseous state even in the shape of a solid-state, and the condition that it is separable with the multi-annular aromatic compound of a gaseous state so that only a multi-annular aromatic compound may be in a gaseous state that is, and fullerene and a multi-annular aromatic compound are separated. as the conditions for this separation -- fullerene -- the shape of a solid-state -- or if it becomes liquid and a multi-annular aromatic compound can exist by the gaseous state, the temperature of arbitration and a pressure can be taken. for example, the bottom of the same temperature as the time of separating a multi-annular aromatic compound from the soot-like matter content air current in the process (2-1) of point \*\* by the gaseous state, and a flow and pressure requirement -- fullerene -- the shape of a solid-state -- or what is necessary is to suppose that it is liquid and just to separate a multi-annular aromatic compound The temperature in this case and a flow and pressure requirement consider economical efficiency, and should just carry it out on the optimal conditions. Especially, it is desirable also in this process (2-2-2) to consider as the desirable range in the same temperature as the time of separating a multi-annular aromatic compound from the soot-like matter content air current in the process (2-1) of point \*\* by the gaseous state and a flow and pressure

requirement.

[0054] Process (2-2-3)

It is the process at which the solubility of fullerene extracts a multi-annular aromatic compound from the shape of a solid-state containing fullerene and a multi-annular aromatic compound, and liquid mixture low at this process (2-2-3), using an organic solvent with the high solubility of a multi-annular aromatic compound as an extracting solvent. this extracting solvent, i.e., the mixed solvent which contains the amides of the carbon numbers 3-5 of the carbon numbers 2-5, such as a ketones; tetrahydrofuran of the carbon numbers 3-5, such as an alcohols; acetone of the carbon numbers 1-4 of a methanol, ethanol, propanol, ethylene glycol, a glycerol, etc. and a methyl ethyl ketone, diethylether, and dioxane, such as ether; N.N-dimethylformamide, and these as an example of a solvent (a poor solvent may be called hereafter) with the low solubility of fullerene, is mentioned. Alcohols are desirable, especially, a with a carbon number of three or less thing is desirable, and especially 2-propanol (isopropyl alcohol) is [ among these ] desirable.

[0055] As solubility of the fullerene C60 of these poor solvents, it is desirable that it is 1g/l. or less, and it is desirable that 100 moremg /or less is [ 1. ] especially 50 or less mg/L. Although it may be directly contacted into the shape of a solid-state of point \*\*, and liquid mixture, generally, a poor solvent dissolves in the organic solvent which the both sides of fullerene and a multi-annular aromatic compound show high solubility, once uses this mixture as a solution, adds a poor solvent to this and deposits fullerene.

[0056] As for the amount of the poor solvent used in this case, it is desirable that it is amount extent of 1 - 30 weight double to the amount of organic solvents used for this solution adjustment also in the amount of 0.1 - 50 weight double. If there are few amounts of a poor solvent, the amount of deposits of fullerene will decrease and recoverable fullerene will decrease. If many [ too ], the container capacity which performs these actuation will become large, and a loss will occur economically. As temperature which mixes a poor solvent, it is -20-150 degrees C, and it is usually desirable especially that it is 30-60 degrees C further 10-80 degrees C -10-100 degrees C. What is necessary is for filtration etc. just to recover the fullerene which deposited by mixing a poor solvent. On the other hand, since most multi-annular aromatic hydrocarbon is dissolved into a solvent, without depositing, the solution after removing fullerene can collect multi-annular aromatic compounds as a solid-state by distilling off the solvent etc.

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**EXAMPLE**

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[Example] Although an example is shown below and this invention is explained to it still more concretely, unless the summary of this invention is exceeded, this invention is not limited to the following examples.

[0058]

[Example 1] 3.8mg of soot-like matter obtained by the combustion method by using toluene as a raw material was heated from the room temperature to 1150 degrees C in 20-degree-C per minute in desiccation nitrogen gas 100 cc/min using the apparatus for thermogravimetry ( TG-DTA6300 by SEIKO CORP.), and change of weight was measured. The obtained result is shown in drawing 2 . In drawing 2 , in a left axis of ordinate, a right axis of ordinate shows the rate of change of the rate of a raw material, and an axis of abscissa shows heating temperature for the rate of loss in quantity to the weight of 3.8mg. A passage clear from the graph which was shown in drawing 2 and which shows weight reduction, and the graph which shows weight rate of change, if temperature becomes 100 degrees C or more, weight will decrease gradually, and it turns out that weight reduction is accelerated from near 400 degree C. And in an elevated-temperature field 500 degrees C or more, the weight of the soot-like matter decreases rapidly. This is that a lot of fullerene in the soot-like matter will sublime if it takes into consideration that the sublimation temperature of fullerene is 400-800 degrees C, and it turns out that the rapid decrease of weight of the soot-like matter arose.

[0059] . Furthermore, qualitative analysis of the gas constituents generated when the soot-like matter was heated was performed on condition that the following using the quadrupole form mass spectroscope (two to JEOL auto mass AM15 mold). A result is shown in drawing 3 .

A measuring method : The EI method furnace section temperature : 290 degrees C Transfer tube temperature : 285-degree-C GC oven temperature : 285-degree-C interface temperature : 285-degree-C ionization chamber temperature : 260-degree-C photograph mull electrical potential difference : 450V ionizing voltage : 70eV ionization current : 300microA mass range: 10 - 400amu scan speed : 1000msec  
[0060] In drawing 3 , an axis of ordinate shows the relative intensity of an ion spectrum, and an axis of abscissa shows heating temperature. From drawing 3 , the peak which shows existence of multi-annular aromatic compounds, such as aromatic compounds, such as benzene (molecular weight 78), toluene (molecular weight 92), and a xylene (molecular weight 106), and naphthalene (molecular weight 128), an anthracene (molecular weight 178), was checked in the temperature requirement lower than the sublimation temperature of fullerene in the gas which heated the soot-like matter and occurred. As for this, a multi-annular aromatic compound also shows that it is separable by the gaseous state as well as aromatic compounds, such as benzene. Fullerene and/or a multi-annular aromatic compound are separable from the fullerene and the multi-annular aromatic compound which were obtained by the combustion method, and the soot-like matter containing a carbon system macromolecule component by the gaseous state with the above example. Therefore, from the air current containing such soot-like matter, it is possible to separate fullerene and/or a multi-annular aromatic compound by the gaseous state continuously, and fullerene is continuously understood are disengageable from the air current containing this soot-like matter.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] The whole example outline sectional view of the fullerene composition decollator concerning this invention.

[Drawing 2] Drawing having shown the weight reduction at the time of heating the soot-like matter.

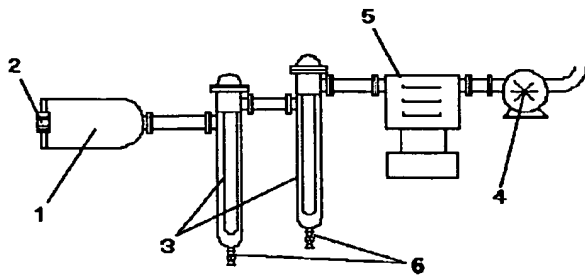
[Drawing 3] Drawing showing the qualitative-analysis result of the gas which occurred when the soot-like matter was heated.

[Description of Notations]

- 1: Fullerene generation equipment
- 2: Burner
- 3: Decollator
- 4: Decompression device
- 5: Deposit equipment
- 6: Recovery system

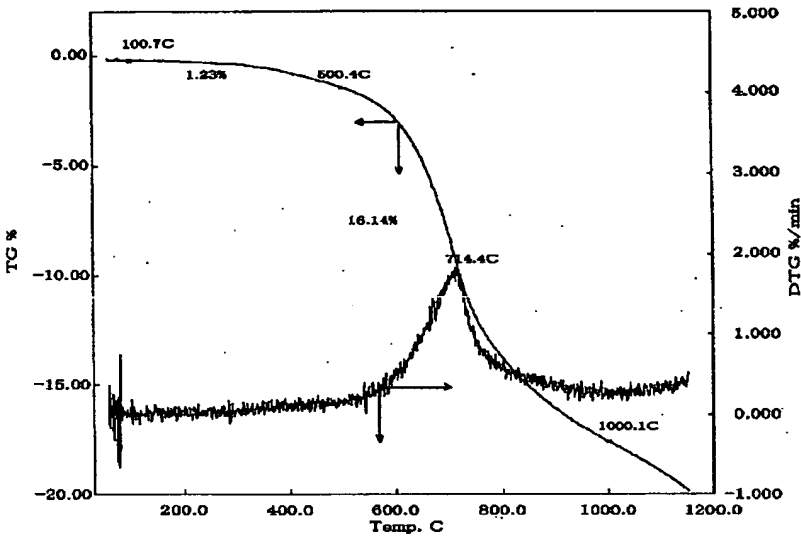
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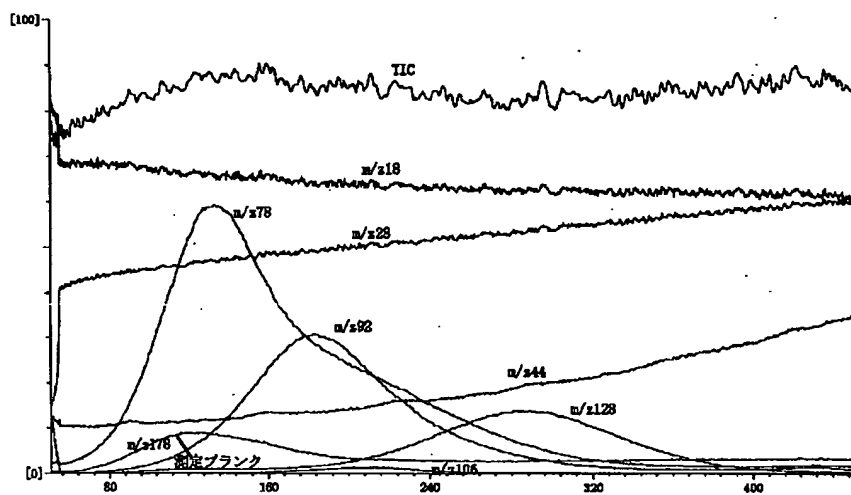


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